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Nanotechnology: Ferrofluids to Liquid Crystals

Nanotechnology: Ferrofluids and Liquid Crystals

Objective

- To synthesize an aqueous ferrofluid (magnetite) and observe its properties.
- To understand how nanotechnology affects everyday life.
- To learn about surfactants and how they work.

Grading

- Pre-Lab (10%)
- Lab Report Form (80%)
- TA Points (10%)

Background Information

Nanotechnology is the science of controlling matter with dimensions between 1 and 100 nanometers. This includes manipulating individual molecules. It is a multidisciplinary field consisting of physics, biology, chemistry, medicine, engineering, and nearly any other applied science. The prefix nano- means ten to the minus ninth power, or one billionth. There have been great advances in nanotechnology in recent years, and scientists routinely make materials that are only a few nanometers in size, or about 1/80,000 the diameter of a human hair. See Figure 1 to notice how small a nanometer is compared to other common materials.

Materials at the nanoscale exhibit interesting optical, electronic, physical, and chemical properties due to their small size. For example, catalysis chemical reactions occur at the surface of bulk material so as particles become smaller, the ratio of the surface area to the volume of the particles increases, thereby making a volume of nanoparticle catalysts more reactive than an equal volume of bulk catalyst. Optical properties of bulk materials are not size dependant, that is no matter what the size of a piece of bulk material it will have the same optical properties. This is not the case for nanomaterials. As you will see in the instructor demo, different sizes of gold nanoparticles exhibit very different colors.

In the 1960s NASA Research Centers discovered fluids that could be controlled through the application of a magnetic field. These fluids were developed to confine liquids in space. These nanoparticle fluids are commonly known as ferrofluids and they are still an active area of research.

Ferrofluids have many current industrial applications. They are used to dampen vibration in audio loudspeakers, they can behave as liquid O-rings in rotating shaft seals, and they are used in high-speed computer disk drives to eliminate impurities. They also have many potential applications in biomedical, environmental, and engineering fields.

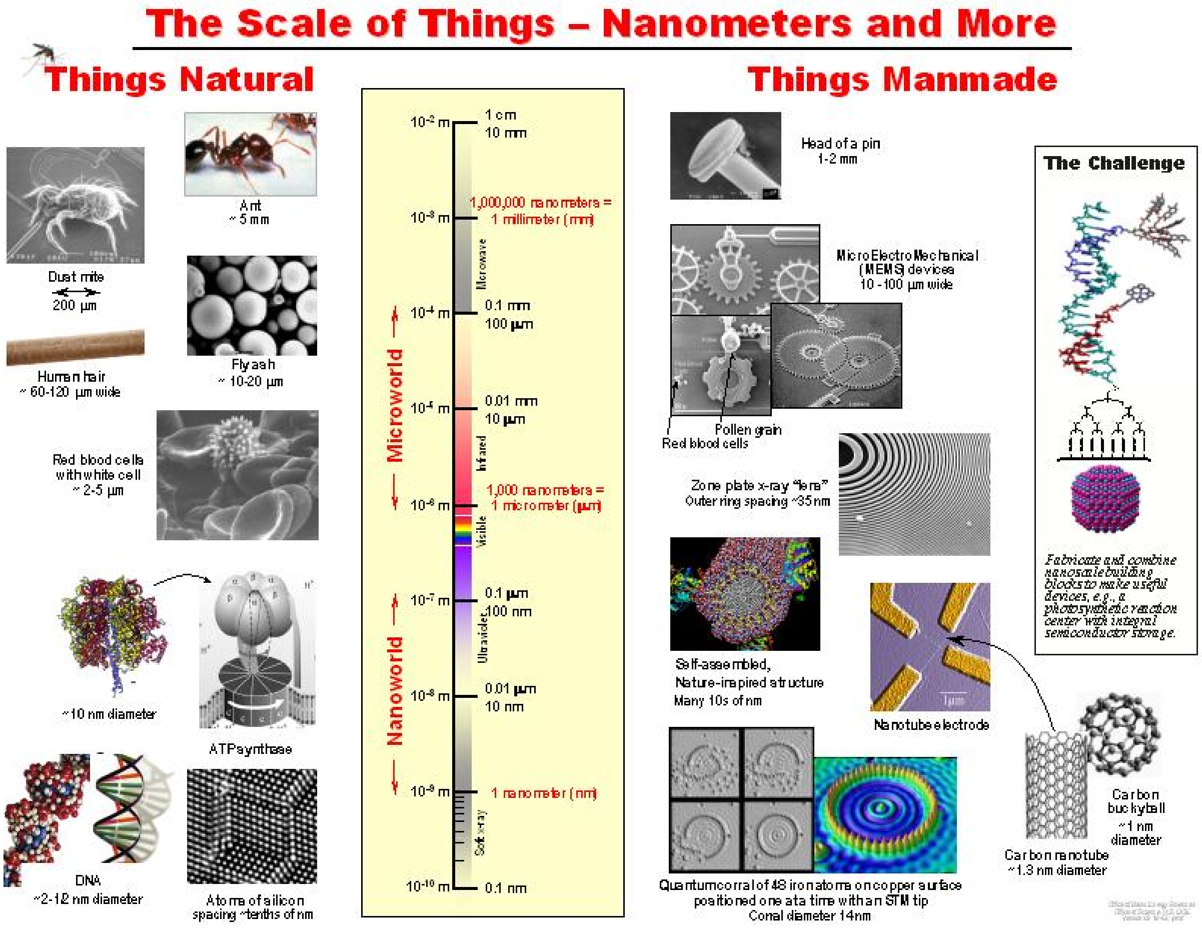

Figure 1-Obtained from Office of Basic Energy Sciences, US Department of Energy

A ferrofluid is a stable colloid suspension of magnetic nanoparticles in a liquid carrier. The nanoparticles are suspended throughout the liquid and have an average size of ~10 nm. It is critical that the nanoparticles are coated with surfactant to prevent the particles from aggregating together. The surfactants must be strong enough to prevent agglomeration even when a magnetic field is applied and they must overcome the intermolecular forces between the nanoparticles. For this reason, a typical ferrofluid contains 5% magnetic nanoparticles, 10% surfactant, and 85% carrier fluid by volume.

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http://cnx.org/GroupWorkspaces/wg897/m15768/Nano2.jpg]

There are two basic steps in creating a ferrofluid: synthesis of the magnetic solid, magnetite (Fe_3O_4), and suspension in water with the aid of a surfactant. The magnetic particles must be very small on the order of 10 nm (100 Å) in diameter, so that the thermal energy of the particles is large enough to overcome the magnetic interactions between particles. If the particles are too large, magnetic interactions will dominate and the particles will agglomerate. The magnetite will be synthesized by a precipitation reaction that occurs upon mixing FeCl_2 and FeCl_3 with ammonium hydroxide (an aqueous solution of ammonia, NH_3). The unbalanced equation for this reaction is as follows:

$$\_\_\mathrm{FeCl}_3 + \_\_\mathrm{FeCl}_2 + \_\_\mathrm{NH}_3^+ + \_\_H_2O \rightarrow \_\_\mathrm{Fe}_3O_4 + \_\_\mathrm{NH}_4\mathrm{Cl}$$

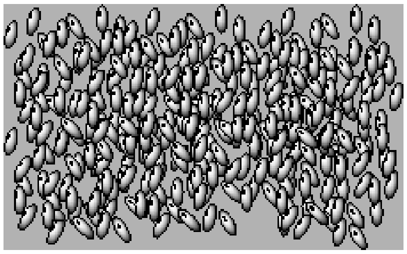
The surfactant used in this synthesis is tetramethylammonium hydroxide ($N(\mathrm{CH}_3)_4\mathrm{OH}$). The hydroxide (OH^-) ions formed in solution tend to bind to the iron sites on the magnetite particles, creating a net negative charge on each particle. The positively-charged tetramethylammonium ions will then associate with the negatively-charged magnetite particles, forming a kind of shell around each magnetite particle. This charged shell raises the energy required for the particles to agglomerate, stabilizing the suspension.

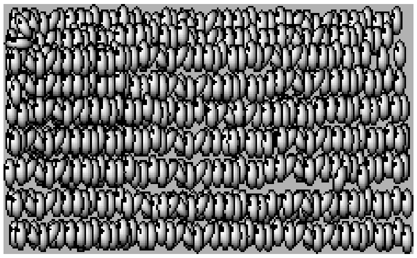
With the help of nanotechnology, liquid crystal displays have become very popular in recent years. Liquid crystal displays (LCD) were first produced by RCA in 1971 and are composed of two glass plates with a liquid crystal material between them. The liquid crystal material is an organic compound that is in a state between a liquid and a solid. Their viscosities are similar to those of liquids and their light scattering and reflection properties are similar to solid crystals. Liquid crystals must be geometrically highly

anisotropic (having different optical properties in different directions)- usually long and narrow -but also become an isotropic liquid (same optical properties in all directions) through a stimulus such as a magnetic field, electric field, temperature, or pressure.

Liquid crystals have several common phases. The simplest liquid crystal phase is called the nematic phase where the molecules spontaneously order with long axes roughly parallel. It is characterized by a high degree of long range orientational order but no translational order. An uniformly aligned nematic has a preferred direction, often described in terms of a unit vector called the director. The type of phase that a liquid crystal possesses ultimately determines its applications.

Note: Is it really necessary to describe the smetic phase? Many of the students were confused by this.l





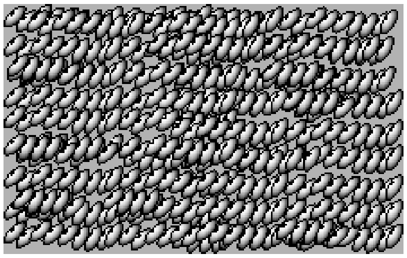
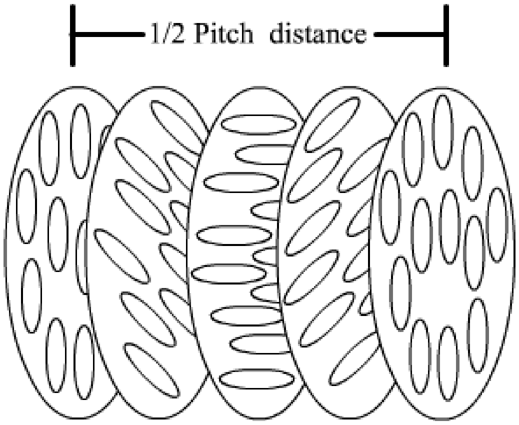
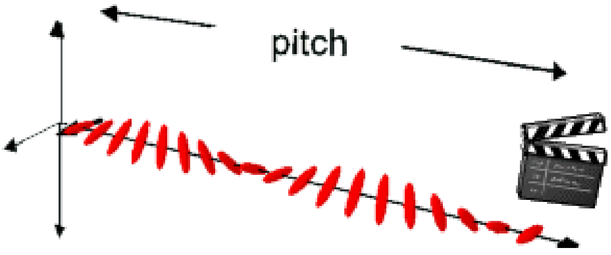


Figure 2 Nematic, smectic-A, and smectic-C liquid crystal phases

A subclass of nematic phases that will be investigated in this lab due to its pressure and temperature sensitive properties is the cholestric phase. The distance over which the director rotates to equal 360° is referred to as the chiral pitch and is normally on the order of a few hundred nanometers, or precisely the wavelength of visible light. This allows liquid crystals to selectively reflect light of wavelengths equal to the pitch length, so that a color will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum. Changes in the director orientation between successive layers modifies the pitch length resulting in an alteration of the wavelength of reflected light according to the temperature. The angle at which the director changes can be made larger, and thus tighten the pitch, by increasing the temperature of the molecules, hence giving them more thermal energy. Similarly, decreasing the temperature of the molecules increases the pitch length of the chiral nematic liquid crystal. This makes it possible to build a liquid crystal thermometer that displays the temperature of its environment by the reflected color.





Experimental Synthesis

Part I. Synthesis of Gold Nanoparticles (DEMO)

Chemicals

1.0 mM $HAuCl_4$ (stored in amber bottle)

- 1% trisodium citrate dihydrate solution

Nanoparticle Synthesis

- Add 20 mL of 1.0 mM $HAuCl_4$ to a 50 mL Erlenmeyer flask on a stirring hot plate. Add a magnetic stir bar and bring the solution to a boil

> **Note:** The TA's need to be told to add the citrate as soon as the reaction boils or the solution turns colorless.

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- Add 2 mL of 1% trisodium citrate dihydrate solution and observe the properties.

Part II. Synthesis of the Aqueous Ferrofluid (Procedure modified from J. Chem. Edu. 1999, 76, 943-948.)

Chemicals

1 M $FeCl_3$ in 2 M HCl Solution:

2 M $FeCl_2$ in 2 M HCl Solution

- 25% tetramethylammonium hydroxide in water

1.0 M NH_3 Solution: Dilute at least 200 mL of concentrated ammonium hydroxide with water to 3.0 L) Open containers of ammonia are odorous and their concentration will decrease over periods of time.

CAUTION: Ferrofluids can be messy. This particular ferrofluid will permanently stain almost all fabrics. Also DO NOT LET THE MAGNETITES TOUCH THE SURFACE OF THE MAGNET DIRECTLY.

Magnetite Synthesis

- In a hood, place 4.0 mL of 1M $FeCl_3$ and 1.0 mL of 2M $FeCl_2$ solution into a 100 mL beaker. Stir on a magnetic stir plate.
- While stirring, slowly add 50 mL of 1.0 M aqueous NH_3 solution over a 5 minute period using a buret. Initially a brown precipitate will form followed by a black precipitate, which is magnetite.
- CAUTION: Even though 1M NH3 is fairly dilute, NH_3 is a strong base.
- Remove from stirring and immediately use a strong magnet to work the stir bar up the walls of the beaker. Remove the stir bar with a gloved hand being careful not to let it touch the magnet.
- Allow the magnetite to settle, then decant off the clear liquid into a waste beaker without losing a large amount of precipitate. The settling process can be expedited by placing a strong magnet below the beaker.
- Transfer the solid to a plastic weighing boat. Rinse out the beaker with a wash bottle.
- Use a strong magnet to attract the ferrofluid to the bottom of the weigh boat. Carefully decant as much clear liquid as possible into the waste beaker. Rinse again with water from the wash bottle and decant. Repeat the rinsing process a third time. What are you removing by rinsing?
- Add 1-2 mL of 25% tetramethylammonium hydroxide. Gently stir the solution with a glass stir rod for at least a minute to suspend the solid in the liquid. Use a strong magnet to attract the ferrofluid to the bottom of the weigh boat. Pour off and discard the dark liquid. Move the strong magnet around and again pour off any liquid. If the ferrofluid

does not produce spikes, continue to move the strong magnet around, pouring off any liquid.

Ferrrofluid Properties

1. Hold a magnet underneath the weigh boat that contains the ferrofluid. Move the magnet around the underside of the weigh boat. Move the magnet close to and far from the weigh boat. Record your observations
2. Add a couple of drops of ferrofluid to a small piece of clean paper. Let the solution dry. Once it is dry, bring a strong magnet close to the paper. What happens?
3. Use several different magnets to observe the properties of the ferrofluid and record your observations in your notebook.

Part III. Synthesis of Cholesteryl Ester Liquid Crystals

Chemicals

- Cholesteryl oleyl carbonate
- Cholesteryl pelargonate

- Cholesteryl benzoate
- Vials
- Heat gun

Liquid Crystal Synthesis

1. Place 0.65 g cholesteryl oleyl carbonate, 0.25 g cholesteryl pelargonate, and 0.10 g cholesteryl benzoate in a vial.
2. In a hood, with the cap off, melt the solid in with a heat gun.

3. While the mixture is still a liquid, divide it into separate vials using a disposable pipette. Put the caps back on the vials. Allow the vials to cool and observe their properties.
4. Clean up your bench area.
5. Listed below is a chart of the different ratios that produce liquid crystals with different transition temperatures. Placing liquid crystals with different transition temperatures next to each other on a clear piece of contact paper makes it possible to make a thermometer.

Cholesteryl oleyl carbonate (g)	Cholesteryl pelargonate (g)	Cholesteryl benzoate (g)	Transition range, degrees C
0.65	0.25	0.10	17-23
0.70	0.10	0.20	20-25
0.45	0.45	0.10	26.5-30.5
0.43	0.47	0.10	29-32
0.44	0.46	0.10	30-33
0.42	0.48	0.10	31-34
0.40	0.50	0.10	32-35
0.38	0.52	0.10	33-36
0.36	0.54	0.10	34-37
0.34	0.56	0.10	35-38

0.32	0.58	0.10	36-39
0.30	0.60	0.10	37-40

Pre-Lab: Nanotechnology

(Total 10 Points)

Hopefully here for the Pre-Lab

Note: In preparing this report you are free to use references and consult with others. However, you may not copy from other students' work (including your laboratory partner) or misrepresent your own data (see honor code).

Name(Print then sign): ____

Lab Day: __________________Section: ________TA_________________________

Part I. Demo of Gold Nanoparticles

1. In a 3 nm gold particle, what percentage of the atoms are on the surface? Hint: You need to find the radius of a single gold atom and the equation for the volume of a sphere is also helpful.Remember that the volume of a shell is Vshell=4/3πr3 (r3-(r-2r)3).

> **Note:**I am giving them this because all the students had trouble with this. The other things are easier to find but this isn't.

Part II. Synthesis of an Aqueous Ferrofluid

1. How would you make a 100 mL solution of 1.0 M $\mathrm{FeCl_3}$ in 2.0 M HCl from $\mathrm{FeCl_3} \cdot 6\mathrm{H_2}O$ and concentrated HCl solution? Show all calculations. Hint: First find volume of water needed to make concentrated HCl ~12.1 M

Part III. Liquid Crystal Synthesis

1. In your own words, explain what a liquid crystal is.

Report: Nanotechnology

On my honor, in preparing this report, I know that I am free to use references and consult with others.

Hopefully here for the Report Form

Note: In preparing this report you are free to use references and consult with others. However, you may not copy from other students' work (including your laboratory partner) or misrepresent your own data (see honor code).

Name(Print then sign):
____

Lab Day: _______________________Section:
__________TA________________________________

Part I. Demo of Gold Nanoparticles

1. What was the starting color of the $\mathrm{HAuCl_4}$ solution?

1. What was the beginning oxidation state of Au?

1. What was the ending oxidation state of Au?

1. What is the purpose of the sodium citrate solution?

1. What is the total surface area of 3 g of 5 nm gold particles assuming gold has a density of $9.3 \mathrm{g}/\mathrm{cm}^3$?

1. What is the total surface area of 3 g of 5 micrometer gold particles assuming gold has a density of $9.3 \mathrm{g}/\mathrm{cm}^3$?

Part II. Synthesis of an Aqueous Ferrofluid

1. Write out the over-all balanced equation for the ferrofluid synthesis.

1. Why did we rinse the nanoparticles three times with water (what are you specifically removing)?

1. What is the purpose of the surfactant? Chemically explain the process.

1. Other than those listed, what are three uses for ferrofluids.

Part III. Liquid Crystal Synthesis

1. As the color of the liquid crystal changes, what is happening to the pitch length?

1. If the color is green and changes to red, chemically/physically explain what has happened to the liquid crystal and be specific..Hint: Look at the wavenmber values assigned to each color. Does this correspond to a temperature increase or decrease? Why?

1. A student measures 0.66 g cholesteryl oleyl carbonate, 0.69 g cholesteryl pelargonate, 0.15 g cholesteryl benzoate and combines them to make a liquid crystal. What is the most likely transition temperature?

Thermochemistry

Thermochemistry

We will begin lab in the amphitheatre of DBH

Objective

- To explore heat transfer through calorimetry.
- To use calorimetry to determine the enthalpy of reaction of a strong acid and a strong base.
- To use Hess's Law of Heat Summation to determine the heat of hydration in calcium chloride.
- To explore a common use of heat of reaction in real life.

Grading

- Pre-Lab (10%)
- Lab Report Form (80%)
- TA Points (10%)

Background Information

When two objects at different temperatures are brought into physical contact, thermal energy will spontaneously transfer from the warmer object to the colder object until both objects have achieved the same temperature. Assuming the two objects are thermally insulated from their surroundings, the heat lost by the warm object is identical to the heat gained by the cold object. This is a manifestation of the Law of Conservation of Energy.

The heat transfer, q, is a function of the mass of the object (m), the change in temperature undergone by the object ( ) and the object's specific heat

( ). This statement can be expressed mathematically as

q =

Temperature change is always defined as - , which means that q for the hotter object ( ) is negative and q for the colder object ( ) is positive. If energy is conserved, then

+ = 0

and

( ) + ( ) = 0

Now consider dropping an ice cube into water just warm enough to melt the ice cube but not warm enough to further heat the water from the cube. The observation is that the ice cube melts and the warm water cools to C. It is important to recognize that during the phase change, the temperature of the ice cube does not change. Therefore, it is not possible to use the preceding equation to determine the heat transferred. Rather, the energy transferred to the ice cube from the warm water affects the phase change. The energy equation is now adjusted to incorporate the enthalpy required to melt the ice cube, (where f stands for fusion):

( ) + = 0

It is also possible to have thermal energy when chemical reactions occur. The amount and direction of heat flow is dependant on the chemicals reacting. Using a calorimeter, it is possible to experimentally determine the heat of reaction.

Calorimetry

In the technique known as constant-pressure calorimetry, enthalpies of phase changes or chemical reactions are determined indirectly by measuring temperature (at constant pressure) changes in a medium, most often water, surrounding the materials undergoing the change. That is, by measuring of the water one can use the preceding equation to calculate for the process of interest. Of course, this means one must know the mass of the water used and water's specific heat: = 4.18 J/(gK).

Today in Part I, you will add a strong base to a strong acid, measure the temperature change in the water as the two react, and use that information to calculate the heat of reaction per gram of NaOH. Then convert your experimental value into an enthalpy in kJ/mol (of NaOH).

The enthalpy of a reaction might be difficult to obtain directly by experiment but can be determined by measuring (or looking up in tables) the enthalpy changes of reactions which contain the reactants and products in a process governed by Hess's Law of Heat Summation. In Part II of this experiment you are asked to find the enthalpy of hydration of the "target reaction" in this manner.

Target reaction:

It cannot be measured directly because of the slow kinetics of the reaction in the solid state. However, the heats of dissolution of and can be determined and, using Hess's Law, the enthalpy of hydration can be calculated.

Theoretical value of the enthalpy of hydration of anhydrous is -81.33kJ/mol. Theoretical value of the enthalpy of hydration of is 15.79 kJ/mol.

Experimental Procedure

Materials Required

- two Styrofoam cups (serve as the calorimeter)
- styrofoam cover (top to the calorimeter)
- conventional or digital thermometer
- stirring motor and stir bar
- two large Ziploc bag
- two plastic spoons

Setup of the MicroLab Thermistor

- Open the MicroLab Program by clicking on the Shortcut to MicroLab.exe tab on the desktop.
- On the “Choose an Experiment Type” Tab, enter a name for the experiment, and then double click on the MicroLab Experiment icon
- Click “Add Sensor”, Choose sensor = Temperature (thermistor)
- Choose an input, click on the red box that corresponds to the port that your thermistor is connected to.
- Label = Thermistor, sensor units = , click next
- Click “Perform New Calibration”
- Click “Add Calibration Point” place the thermistor and thermometer in an ice water bath. Wait until the temperature is constant and then read the temperature on the thermometer (to the nearest 0.1) and enter it into the “Actual Value” box in MicroLab and hit “ok”.
- Again, Click “Add Calibration Point” place the thermistor and thermometer in warm water bath. Wait until the temperature is constant and then read the temperature on the thermometer (to the nearest 0.1) and enter it into the “Actual Value” box in MicroLab and hit “ok”.
- Under Curve Fit Choices , click on “First order (linear)” and then “Accept and Save this Calibration”, when prompted to enter units, set as deg C. Save as your name-experiment-date.
- Click “Add Sensor”, Choose sensor = Time
- Choose an input, click on the red box that corresponds any of the Timers.
- Label = Time 1, click next, click Finish.
- Left click on thermistor and drag to the Y-axis over “data source two”, also click and drag to column B on the spreadsheet and also click and drag to the digital display window.
- Left click on Time and drag to the X-axis over “data source one”, also click and drag to column A on the spreadsheet and also click and drag to the digital display window.
- When you are ready to obtain data, click start. When you are finished collecting data, click stop. To run another trial, click repeat experiment.

Part I. Reaction of Strong Acid with Strong Base

1. Weigh the calorimeter (styrofoam cups with lid) WITH a stir bar. Accurately measure 50 mL of 1 M HCl into your calorimeter. Turn on the stirring motor to the medium speed. Fit the thermistor though the cardboard lid to a length such that its tip goes deep into the solution but misses the stir bar. Cover the calorimeter.
2. Start the Acquisition program. You should see successive, constant temperature readings of near room temperature. Accurately measure 50 mL of 1 M NaOH and quickly add it to the acid solution in the Styrofoam cups. Cover the calorimeter.
3. Continue monitoring the temperature change until thermal equilibrium is reached (the temperature stops changing or starts decreasing).
4. Stop the Acquisition program. SAVE YOUR FILE. Remove the cardboard lid, reweigh the calorimeter and record the information on your lab report.
5. Repeat the same procedure (Steps 1-4) two more times. Save all your files. Give them different, distinguishable names.

Print off your graphs and use the data to determine the initial and final temperatures. Record all the temperatures to the nearest 0.1 . If a slight downward trend appears on the final temperature plateau, use the maximum value achieved. Calculate the average enthalpy of the reaction and standard deviation for the three trials. Then combine your data with the data obtained from the rest of the group and calculate average enthalpy of the reaction and standard deviation for all trials together. Compare your average and standard deviation with that of the larger set and comment on the results obtained using a larger data set.

Part II. Enthalpy of Reaction

[link]

The same basic procedure you used in the dry ice sublimation lab will be used here today.

1. Tare your calorimeter and pour approximately 75 mL of cold water in it. Add stir bar. Record the mass to 3 decimal places. Place the cups on the magnetic stirrer and turn on the stirring motor to a medium rate. Make sure you can fit the thermistor though the styrofoam cover to a length such that its tip goes deep into the water but misses the stir bar but do not insert it. Cover the calorimeter.
2. Start recording data on the MicroLab interface. Let it run for about 10 seconds before putting thermistor through the Styrofoam cover. You should see successive, constant temperature readings of near room temperature. Approximately 5 grams of anhydrous has been weighed for you, record the weight of this plus the weight of the weighing bottle. Then weigh the dry empty weighing bottle. Quickly add to the water and reposition the thermistor and cover assembly.

Note: Since anhydrous absorbs moisture rapidly from the air, close the lids of the bottles securely immediately after using. Dry the spatula each time before weighing the powder and clean the balance of any solid.

1. Continue monitoring the temperature change until thermal equilibrium is reached (the temperature stops changing or starts decreasing).
2. Stop collecting and SAVE YOUR DATA and/or print it.
3. Repeat steps 1-4 two more times. Don’t forget to save your data each time you do a run because it is lost as soon as the next run begins.
4. Repeat the process but replace anhydrous with .
5. Use the data to determine the initial and final temperatures. Record all temperatures to the nearest 0.1 . If a slight downward trend appears on the final temperature plateau, use the maximum value achieved. Calculate the average enthalpy of dissolution and standard deviation. Use Hess’s Law to calculate the heat of hydration of and % error. Then combine your data with the data obtained from the rest of the class and calculate the average enthalpy of dissolution and hydration.

Calculations

Calculations are similar to those done for the acid-base neutralization reaction. The calculation of is the same as the calculation of , that is:

=

qwater can be calculated using water’s specific heat, mass of water and temperature change of water solution:

In order to account for the mass of anhydrous or hexahydrate, divide by the mass of anhydrous or to get in J/g. Then convert to J/mol.

Part III. Chemistry of Life

Hot packs and cold packs are a real life example of thermochemistry. Anhydrous magnesium sulfate and ammonium chloride can be used to make “hot/cold” packs similar to those used for sports injuries and in hospitals. Your TA will make a pack from each of the two compounds and pass them around and answer some fundamental thermochemical questions about the reactions involved.

TA Procedure

- Fill two Ziploc bags half way full with water.
- Put two spoons full of anhydrous magnesium sulfate into one bag and two spoons full of ammonium chloride into the other bag, zip them closed, and shake.

Pass the packs around to students and observe the temperature change.

Forensics Lab

Forensic Lab

Objective

- To appreciate the variety of tests available to the Forensic Scientists
- To observe latent fingerprinting development
- To studyink identification
- To do a breathalyzer analysis

Introduction

Part 1. Latent Fingerprint Development

The earliest recognition of the uniqueness of fingerprints and their suitability for personal identification came from the ancient Chinese, who employed a thumbprint in lieu of a signature on legal conveyances and even criminal confessions. Since literacy was uncommon, this proved a practical measure. The first scientific recognition of fingerprints in the West came in the 17th century, when the first studies on fingerprints were published in England and Italy. Two hundred years later Sir Francis Galton published a book, Finger Prints, were he proposed that no two fingers have identical ridge characteristics and fingerprints remain unchanged during the individual’s lifetime. Today the practice of utilizing fingerprints as means of identification is an indispensable aid to modern law enforcement.Fingerprints have been the reason for the solving of a vast amount of cases. Crime scene fingerprints fall into three types:

1. Patent or visible impressions occur as the result of transferring a foreign material (paint, grease, blood or ink) coating the skin of the fingers to the object.2. Plastic or molded impressions are deposited when the hands, fingers or feet are pressed into a soft rubbery type material (wax, putty, clay or tar) that will retain the impression of the ridge pattern in this material.3.

Latent or hidden impressions are left on polished surfaces such as wood, metal or glass by the sweat-moist ridges of the fingertips. Since latent fingerprints are not visible to the naked eye, they need to be developed using one of the following techniques:

‘Powder and brush’ technique: The surface is dusted with a very fine powder that sticks to the oils and perspiration that are left behind from the friction ridges of the skin. Some surfaces, however, absorb this powder and the fingerprints are not identifiable.

Laser luminescence: Involves illumination of fingerprints which fluoresce due to particles picked up during everyday life such as paints, inks and oil. It can be used on metals, plastic, cloth and wood.

Ninhydrin test: Indantrione hydrate is sprayed onto the fingerprint where it reacts with the amino acids, giving a dark purple deposit. It can be used to develop very old prints (made over 30 years ago).

Iodine vapor: Can be used to develop fingerprints on fabrics and rough surfaces. Iodine vapor alone is useful only for prints up to 24 hours old, however a mixture of the vapor with steam allows this method to be effective for up to two months. Prints developed by this method disappear rapidly, so it works well in situations where you want to conceal your work.

Most fingerprint development techniques are based on specific chemical reactions between the oily residues of a latent print and an applied chemical. The product of the reaction will have a new composition that is more visible and can be photographed to compare to other prints. A simple chemical method for fingerprint development is cyanoacrylate fuming.

The active ingredient in superglue is cyanoacrylate. To cure for adhesive applications, it only needs hydroxyl ions, which are found in any trace amounts of water making superglue applicable to most materials. With the help of water, cyanoacrylate molecules undergo anionic polymerization to make a very strong plastic mesh. In crime scene investigations, superglue reacts with the traces of amino acids, glucose, sweat, fatty acids, and proteins in the latent fingerprint and the moisture in the air to produce a visible, sticky white material that forms along the ridges of the fingerprint. The final result is an image of the entire latent fingerprint.

In order for cyanoacrylate to react with amino acids and sweat, it must be in the gaseous state. It has a boiling point between 49 °C and 65 °C so low heating can vaporize it. The presence of moisture in the air can expedite the reaction with the latent print. The main components of the vaporizing chamber will be shown under procedure; a) glass dish to contain fumes b) vial with water to provide moisture c) hot plate on low heat and d) bottom of aluminum can to hold superglue.

Silver nitrate: Silver nitrate reacts with chlorides in the fingerprints, to give the insoluble salt, silver chloride, which rapidly turns black on exposure to light. This method is not suitable for fabrics or rough surfaces.

After developing the latent impression it is photographed and lifted with a clear tape to be placed on a backing card with a contrasting background. It can then be entered into a computer, which allows it to be quickly and easily recalled and compared to the fingerprint of a suspect. Identification depends on showing a minimum of twelve matching characteristics in the ridge pattern. When these points of comparison are shown, it is considered that the proof of identity has been established.In this lab you will be developing your fingerprints using 2 methods: the first uses iodine vapor whereas the second uses fuming cyanoacrylate

Part 2. Identification of Inks

In document examination, the examination of inks often plays an important part. As a rule, the examination centers on the question as to whether the ink of certain passages or of alternations in the text is identical with the ink found in the possession of the suspect. For this reason the examination of questioned documents seldom consists of a complete determination of the inks in question but is usually restricted to a comparative examination of certain properties of these inks.Many different nondestructive techniques of the examination of inks are available: reflected infrared radiation, reflectance microspectrophotometry, lasers and scanning electron microscopy. Unfortunately, the reflectance methods are often subject to interference effects from “bronzing” or “sheering” of the ink.Semi-destructive methods involve high-performance liquid chromatography (HPLC) and thin layer chromatography (TLC). Most chromatographic techniques are based on the minute sampling of a single written character representative of the questioned text. Small samples of ink bearing paper are removed from the document, they are then extracted with a suitable solvent, and the components of the solution are separated using HPLC and TLC. If the inks being compared show different composition, they did not come from the same pen.In this lab you will be separating dyestuffs of several ballpoint pens using thin layer chromatography. Comparison of the dye composition will allow you to find out which pen was used by your TA to spot the TLC plate.

Part 3. Invisible Ink

Invisible ink has been used to conceal secret messages for a long time. Many different liquids can be used as invisible inks such as lemon juice, milk, vinegar or a solution of phenolphthalein.

Part 4. Breathalyzer

To determine whether a driver is driving under the influence of alcohol, law enforcement officers perform a Breathalyzer test to measure the blood alcohol content of the bloodstream. In the breath analyzer test, a breath sample is passed through a solution containing acidified potassium dichromate , which is bright yellow. Potassium dichromate, a strong oxidizing agent, oxidizes ethyl alcohol to acetic acid (vinegar). The chromium is consequently reduced from the VI to the III oxidation state, which is green. The unbalanced equation for this reaction is

Equation:

The amount of alcohol in a breath analyzer sample is therefore proportional to the amount of potassium dichromate that is used up and also therefore to the loss of yellow color.

The Blood Alcohol Concentration (BAC) may then be calculated from the equation

BAC = 0.8 A/WR

Where W is a body weight of the individual being tested, A is the amount of alcohol in the body (in mL) and R is a “Widmark R Factor”, approximately 0.68 for men and 0.55 for women.In most states, a BAC of 0.1 percent is sufficient to be convicted for driving under the influence of alcohol; in some states the threshold BAC is even lower.

Part 5: Blood Stain Analysis Using Chemiluminescence

Investigators often find bloodstains during their examination of a crime scene. They also find stains that could be similar substance, something other then blood, such as red paint. How would you test a stain to see if it is blood? Human blood contains a pigment called hemoglobin, which is used to transport oxygen through our body. This pigment is used by number of tests to identify the presence of blood. One most common test used by investigators that reveals the presence of blood is the Luminol Test. In this test the bloodstain can be made to glow with a blue light due to chemiluminescent reaction of the luminol reagent with the iron (Fe) in the hemoglobin. Chemiluminescence is the reversed case of photoreaction: by a chemical reaction, an excited particle is formed, which looses its energy by producing a light quantum of light. The most important characteristic is that the light is emitted in cold. In other words, chemiluminescence happens when a molecule capable of fluorescing is raised to an excited level during a chemical reaction. Upon its return to the ground state, energy in the form of light is emitted. Luminol is one of the most outstanding molecules that emit appreciable amounts of light.

Experimental Procedure

Part 1a: Latent Fingerprint Development using Iodine vapors

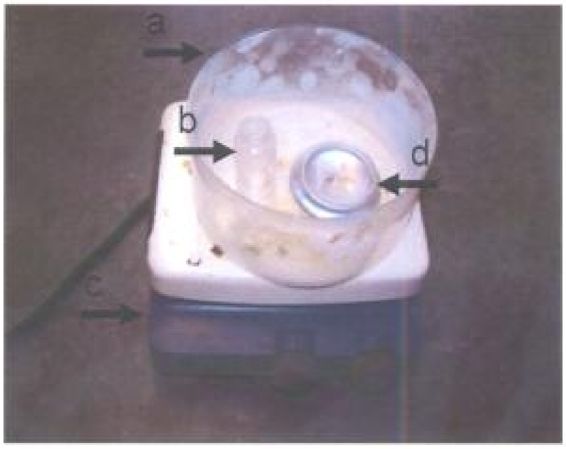
Caution! Iodine vapors are poisonous and should not be inhaled. Keep the jar with iodine in the fume hood at all times.

1. Press you finger onto a piece of filter paper.

2. Using tweezers, place the filter paper into a jar with iodine and recap it.

3. When you can see the fingerprint clearly, remove the filter paper using tweezers and keep it until the end of the lab.

Part 1b: Latent Fingerprint Development using fuming cyanoacrylate.



Materials

Large hotplate

Large glass dish for fuming chamber

Metal Cans (2)

Superglue Water

Glass slide

Experimental Procedures

This experiment should be conducted in the hood

1. Place finger prints on glass slide. Alternately, small objects that contain fingerprints can be placed in the chamber.
2. Make sure one pan has water in it.
3. Place a drop of superglue the size of a nickel onto the other can top.
4. Place glass slide inside the fuming chamber.
5. Turn the hotplate on low and allow the fingerprints to develop for approximately ten minutes.
6. Turn the hotplate off and remove the fingerprint specimen. Allow it to cure for approximately 5 minutes.

Caution! Overheating cyanoacrylate can produce highly toxic hydrogen cyanide gas. The reaction should take place in a well ventilated area with the hot plate on low.

Caution! Superglue can bond instantly to fingers and other body parts. Take caution in using it. In the event of an inadvertent bonding, use acetone to soften the glue.

Part 2: Ink Identification

1. Obtain a precut TLC plate. Do not touch the white surface and handle carefully only by the edges.

2. Using a pencil, draw a light line across the shorter dimension 1 cm from the bottom. Using a ruler as a guide on the line, mark off five equally spaced intervals on the line as shown in Figure 1.

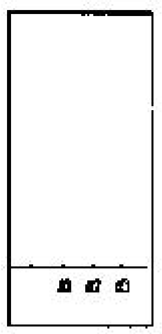


Figure 2. TLC plate

3. Scribble on a small piece of paper with each of the pens and dissolve the ink with a drop of ethanol. The dissolved ink can now be spotted onto a pencil line drawn in step 2. Repeat step 3 for each pen. Do exactly the same procedure for the unknown writing sample that you can obtain from your TA.

4. Use a 400 mL beaker for the development chamber. Add the solvent mixture (ethyl acetate/ethanol/water) to the beaker to a depth of about 0.5 cm. Remember: the level of the solvent must be below the spots on the plate. Using tweezers or forceps, place the spotted plate in the development chamber so that it rests in the solvent and against the beaker wall. Cover the beaker (with a paper towel) and allow the plate to develop. It might take more than 10 min, so you can proceed with Part 3 and Part 4.

5. When the solvent has risen on the plate to within 1 cm from the top, remove the plate from the beaker with tweezers or forceps. Using a pencil, mark the position of the solvent front.

6. Allow the plate to air dry and observe the colored separation. Note how many dye components make up the individual pens.

Part 3: Invisible Ink

8. Using a millimeter ruler, measure the distance that each spot (use the center of each spot for consistency) has traveled relative to the solvent front. Calculate the values for each spot. Part 3: Invisible Ink

Method 1

1. Pour a little milk in a beaker. Soften the point of a toothpick in the milk and write a letter or a message with it. Do not use too much milk otherwise the paper will wrinkle. Let the paper dry completely.

2. Place the piece of paper on a warm hot plate and wait until the message appears.

Method 2

1. Cornstarch has been prepared for you by mixing 1 g of cornstarch with 10 mL of water in a beaker and stir until smooth.

2. Heat the prepared mixture for several minutes. Soften the point of a toothpick in the mixture and write a letter or a message with it. Let the paper dry.

3. To observe the message, place it in a jar with iodine vapor in the hood. Recap the jar and let it stand for more than 1 minute.

Method 3

1. Pour about 5 mL of phenolphthalein solution in a beaker. Soften the point of a toothpick in the solution and write a letter or a message with it. Allow the paper to dry.

2. To read the invisible writing, dip a small piece of cotton wool into the 1 M NaOH solution and carefully wipe the paper (do not rub!).

Part 4: Breathalyzer

Caution! Sodium dichromate is a strong oxidizing agent. Avoid contact with the skin.

1. Pour 2 mL of ethyl alcohol into a test tube and add 2 mL of acidic sodium dichromate solution. Mix gently and record your observations.

Part 5:Luminol Analysis

1. The luminol solution (solution 1) has been prepared for you by dissolving 0.1g of Luminol in 20 ml of 10% NaOH in a 50 ml beaker and diluting this solution to 200ml in your spray bottle and set aside.

2. The fake “blood” solution (solution 2) has been prepared for you by dissolving 0.5g of in 20 ml of 5% hydrogen peroxide solution.

3. In the hood blacked out by construction paper smear some “blood” ($K3[Fe(CN)6]$ in 5% hydrogen peroxide) onto a piece of paper towel with a cotton swab. (make sure you are wearing gloves)

4. Quickly spray the wet “blood” stain with the luminol solution (solution 1) and close the hood to the point that you can barely see at the bottom and record your observation.

Colorful Copper

Experiment 3: Colorful Copper

Objective

- To observe, describe and explain the products of a number of chemical reactions of the transition metal copper.
- To use several techniques in recovering copper from solution.
- To understand the concept of percent yield.

Grading

- Pre-lab (10%)
- Lab Report (80%)
- TA points (10%)

Before Coming to Lab…

- Read the lab instructions
- Complete the pre-lab, due at the beginning of the lab.

Introduction

Copper is a soft metal with a characteristic color that we often call "copper-colored", a bright orange-brown color. Copper is relatively inert chemically; it does not readily oxidize (react with oxygen) in air and is react when exposed to simple mineral acids such as sulfuric or hydrochloric acid. One of the most popular uses of copper is in the computer industry where it is used to build the integrated circuits and chips. It is beginning to replace aluminum for this application due to the resulting decrease in costs. Copper is also good at conducting electricity because it has so many free electrons that allow for the efficient flow of current.

In this lab you will preform a series of reactions with copper and observe a variety of distinctive and colorful products. Most chemical syntheses involve the separation and then purification of a desired product from unwanted side products. The common methods of separation are filtration, sedimentation, decantation, extraction, chromatography and sublimation.

This experiment is designed as a quantitative evaluation of your laboratory skills in carrying out a series of chemical reactions, purification and analyses with copper. You will employ two fundamental types of chemical reactions, namely oxidation-reduction (redox) and metathesis (exchange) reactions to recover pure copper with maximum efficiency. The chemical reactions involved are the following.

Redox:
[1]

*Metathesis:
[2]

Dehydration: [3]

Metathesis: [4]

Redox: [5]

Each of these reactions proceeds to completion and in the case of a metathesis reaction, completion is reached when one of the components is removed from the solution in form of a gas or an insoluble precipitate. This is the case for reactions [1], [2], and [3]. In reactions [1] and [3] a gas is formed and in reaction [2] an insoluble precipitate is formed (Reaction [5] proceed to completion because copper is more difficult to oxidize than aluminum).

Metathesis (Exchange) Reaction Defined in Chapter 4 of your textbook: 'One of the following is needed to drive a metathesis reaction: the formation of a precipitate, the generation of a gas, the production of a weak electrolyte, or the production of a nonelectrolyte.'

Oxidation-Reduction (Redox) Reactions. This involves the loss of electrons from one components and an addition of electrons to the other component as the reaction proceeds (the are transferred from one atom to another). The component that loses electrons is said to be oxidized; the one that gains electrons is then reduced. Such reactions are important for the production of electricity due to the energy produced from an electron transfer.

The percent yield of the copper can be expressed as the ratio of the recovered mass to initial mass, multiplied by 100:

% yield = (recovered mass of Cu/initial mass of Cu) x 100

Experimental Procedure

SAFETY PRECAUTIONS: Wear safety glasses and gloves when handling acids. Work in the fume hood. Acetone and Methanol are Flammable, so keep them away from flames. Avoid breathing any vapors, especially methanol, as it is very toxic.

1. Preheat a hot plate in the fume hood.

2. Place one strip of fine copper wire (Remember to record the actual weight, approximately 0.5 g) in a 250 mL beaker. Bend the copper wire so that it rests on the bottom of the beaker.

3. Slowly add 30 mL of 6 M   . Perform this step in the fume hood, as the gas produced is toxic. You may need to gently heat the solution. Observe the color of the gas and solution. Place a wet paper towel and watchglass over the beaker to dissolve the gas. Ask your TA if you are unsure how to do this.

4. Wait until the copper wire dissolves completely before proceeding.

5. Remove beaker from hot plate with a hot hand. Remove watchglass and paper towel. Be sure that the hood is closed as much as possible at this point to avoid breathing in the gas.

6. Add 100 mL of deionized water (Do not use regular water!)

7. Slowly add 30 mL of 6 M NaOH. Note the color of the precipitate and evolution of heat.

8. Add 2 or 3 boiling chips and carefully heat the solution just to boiling point. Note any color change. While waiting for this solution to heat, begin heating ~200 mL deionized water (in a 400 mL beaker) for the next step.

9. Decant some of the supernatant liquid into a 500 mL beaker (Try not to lose any solid while decanting. It is ok to leave some of the liquid behind.). Add about 200 mL of very hot deionized water and allow the precipitate to settle. Decant once more. What are you removing by washing and decantation?

10. Heat the beaker containing the solid for 20 minutes to reduce the volume of the solution (or until the volume has been reduced by half). Having a more concentrated solution will make the following steps proceed faster.

11. Add 15 mL of 6 M to the black tarry substance in the beaker (not the solution that you have decanted) while stirring with a glass rod. What copper compound is present now?

12. Remove the boiling chips.

13. In the hood, add 5-10 one-inch squares of aluminum foil and 5-10 ml of concentrated HCl, noting any color changes.STIR WELL. An ideal ratio should be 7 pieces of Aluminum to 10 ml of acid but you might need more or less depending on the success of your previous steps. If your solution turns green stop and ask your TA for help. Otherwise, continue to add pieces of aluminum until the supernatant is not blue. Identify what forms on the surface of the aluminum. What is present in the solution? What gas is formed in the reaction? How do you know?

14. When gas evolution has ceased, decant the solution and transfer the precipitate to a preweighed 100 mL beaker and record its mass on your report form. Wash the precipitated copper with about 5 mL of distilled water and allow it to settle before you decant the solution, and repeat the process. Then wash the precipitate with about 5 mL of methanol. Allow the precipitate to settle, and then decant the methanol. Finally, wash the precipitate with about 5 mL of acetone. Allow the precipitate to settle again and then decant the acetone from the precipitate. What are you removing by washing?

15. Then use the microwaves to dry your product. Start with 30 seconds and then try 10 seconds more until it is dry. Be sure to let your product cool before weighing it. Then calculate the final mass of copper and from there the weight and percent yield can be determined. Compare the mass with your initial mass and calculate the percent yield. What color is your copper sample in the final step?

Is it uniform in appearance?

Suggest possible sources of error in this experiment.

Antacids

Analysis of Commercial Antacids

Objectives

- Measure the quantity of commercial antacid required to neutralize a simulated stomach acid (0.15 M hydrochloric acid) and compare the effectiveness of several brands of antacids in neutralizing acids.
- Learn and practice the back-titration method.

Grading

You grade will be determined according to the following:

- Pre-lab (10%)
- Lab Report Form (80%)
- TA points (10%)

Introduction

The parietal cells in the stomach secrete hydrochloric acid at a quite high concentration of about 0.155. The flow of HCl increases when food enters the stomach. When you eat or drink too much, your digestive system may generate too much acid. You may develop a condition called "heartburn" or indigestion. Antacids are swallowed to neutralize this excess acid and "relieve" but not eliminate the condition. The reaction that takes place is an acid/base reaction. A little bit of NaOH might be equally effective, but it's quite rough on the rest of the digestive system, so antacids need to be formulated to reduce acidity while avoiding physiological side-effects. Many antacids use $\mathrm{CaCO_3}$ for this purpose.

In addition to the active ingredient (base), tablets may also contain flavors, sweeteners, binders, fillers, antifoam agents, pain relievers (aspirin), etc. In this experiment, the tablets will be analyzed only for their ability to neutralize acids. The base in antacids varies with the brand. Below is an example of active agents in several brands.

Brand Active Agent	Base
Pepto-Bismol	$\mathrm{BiO(HOC_6}H_4\mathrm{COO)}$
Milk of Magnesia	$\mathrm{Mg(OH)_2}$
Rolaids	$\mathrm{NaAl(OH)_2CO_3}$ (newer tablets: $\mathrm{CaCO_3}$)
Tums	$\mathrm{CaCO_3}$
Alka-Seltzer II	$\mathrm{NaHCO_3}$ and $\mathrm{KHCO_3}$
Maalox	$\mathrm{Mg(OH)_2}$ and $\mathrm{Al(OH)_3}$
Gaviscon	

	$\mathrm{Al(OH)_3}$

Acids are neutralized by these bases as illustrated below.

Equation:

$$\mathrm{BiO(HOC_6}H_4\mathrm{COO)} + 3\mathrm{H^+(aq)} \rightarrow \mathrm{Bi^{3+}(aq)} + H_2O(l) + \mathrm{HOC_6}H_4\mathrm{COOH}(s)$$

Equation:

$$\mathrm{Mg(OH)_2}(s) + 2\mathrm{H^+(aq)} \rightarrow \mathrm{Mg^{2+}(aq)} + 2\mathrm{H_2}O(l)$$

Equation:

$$\mathrm{Al(OH)_3}(s) + H^+\mathrm{(aq)} \rightarrow \mathrm{Al(OH)_2^+(aq)} + H_2O(l)$$

Equation:

$$\mathrm{Al(OH)_2^+(aq)} + H^+\mathrm{(aq)} \rightarrow \mathrm{Al(OH)_2^+(aq)} + H_2O(l)$$

Equation:

$$\mathrm{CaCO_3}(s) + H^+\mathrm{(aq)} \rightarrow \mathrm{Ca^{2+}(aq)} + \mathrm{HCO_3^-(aq)}$$

Equation:

$$\mathrm{HCO_3^-(aq)} + H^+\mathrm{(aq)} \rightarrow \mathrm{CO_2}(g) + H_2O(l)$$

In this simple experiment you will find the neutralizing capacity of various commercial antacid tablets. To test their capacity to neutralize acid, we will first dissolve an appropriate and measured amount of the sample in a simulated stomach environment. This is a solution containing a known quantity of HCl that will react with all of the antacid and still leave some extra HCl. Then we will determine how much of the original HCl remains by titrating it to neutrality with a standardized solution of NaOH. Simple subtraction will reveal how much of the acid was neutralized by the antacid tablet. This general method of analysis is called back-titration.

Note: The standardized solutions of NaOH and HCl have been prepared for you. However you need to understand how and why it is done this way. (See Supporting Information on this) Also see notes on Titration Tips.

If N_A is the number of moles of HCl that we use for dissolving the antacid sample, and N_B is the number of moles of NaOH needed to back-titrate the excess HCl, then N_{sample}, the number of moles neutralized by the sample, is given by:

Equation:

$$N_{\text{sample}} = N_A - N_B$$

Remember that the number of moles in a volume of solution equals the concentration multiplied by the volume. $(n = M \times V)$

Dissolved carbon dioxide is converted into the weak acid, carbonic acid $(H_2\mathrm{CO_3})$ which reacts with NaOH. Although the deionized water is free of most impurities, it does contain dissolved carbon dioxide that must be removed by boiling to give accurate titration results. All of the antacids that you titrate contain carbonates. When you acidify the antacid sample with standard HCl, the carbonates are converted into carbonic acid that must be boiled off in the form of $\mathrm{CO_2}$.

In this experiment you will titrate one commercial antacid twice. Each lab section will compile their results and decide which antacid is the "best buy" in terms of neutralizing ability per dollar. The general approach to this quantitative determination is volumetric.

Experimental Procedure

Part 1: Titration of Antacids

Your TA will randomly assign you one of the commercial brands of antacid tablets and you will analyze two samples of it. Before starting, calculate the acid/base ratio of the tablet that you have been assigned that you will neutralize. Start thinking how this may be an error in your final calculation.

1. Weigh one whole tablet using the analytical balance. Record the mass of the intact tablet.

2. Break or cut the tablet to obtain pieces roughly the size indicated in the table below (e.g.. ½, ⅓, etc.) and weigh two of these pieces separately on sheets of weighing paper. (Don't forget to subtract or tare the weight of the paper.) After weighing, fold over the paper and gently crush the sample fragments using the round portion of your padlock, so it dissolves faster.

3. Use a transfer pipet to dispense 25.00 mL of standardized HCl into a clean 125 mL Erlenmeyer flask and add about 20 mL of deionized water. This solution will be used to dissolve the fraction you weighed of the antacid tablet.

4. Transfer one of the weighted crushed samples (without any spilling) into the flask containing the HCl solution. Repeat for the other weighed fraction in another flask and label each flask (1 and 2) to keep track of which sample and which portion is being titrated.

5. Warm gently to dissolve the sample and then boil solution for about a minute. Some components of the samples may remain undissolved, but these will not cause problems.

6. Let the flaks cool down sitting on the bench for couple minutes, and then cool the outside of the flask with tap water.

7. When room temperature is reached add a few drops of methyl purple indicator solution. The flask should now be purple in color. (If it is green instead of purple, you have used too large a fragment and have neutralized all of the HCl. (In this case add 5mL of HCl and observe the color change. If needed add measured amounts of HCl little by little until solution is purple. Remember to record the amount of HCl added and add to the first 25mL of HCl.)

8. Put a clean magnetic stir bar inside flask and stir solution on stir plate. (It is important that you read Titration Tips in Supporting Information below before you titrate, or you may have to repeat titration several times.)

9. Titrate with your standardized NaOH solution until you reach the endpoint, a change in color from purple to green (or from purple to clear). Some samples may not give color changes as sharp as for the HCl standardizations; for these use your best judgment to estimate the endpoint. Endpoints will generally be sharper for quick titrations than for slow ones.

10. Repeat the above procedure with a new sample of the same antacid. Enter your data in an excel spreadsheet in the workrooms, check the web page later on the week and make a final comment on the overall cost to neutralize one mole of HCl for various brands. THIS IS PART OF YOUR REPORT AND IF DATA IS NOT FOUND ON THE WEB YOU SHOULD CONTACT YOUR TA. (No excuses)

Retail Cost Maximum

Label	Antacid Brand	Price (cents per tablet)	Fraction
B	Walgreens Antacid Tablets	2.66	1/6
C	Titralac Plus	5.99	1/4
D	Titralac	5.89	1/4
J	Tums Regular	2.86	1/6
K	Tums Plus	5.32	1/6
M	Eckerd Antacid	2.19	1/6

*Active ingredient in all of these antacids is $\mathrm{CaCO_3}$.

Supporting Information on Standardization:

Molarity is the most commonly used concentration term when one is interested in the amount of materials involved in a chemical reaction in solution. Molarity (M) is defined as the number of moles of solute per liter of solution.

M = $\frac{\mathrm{moles(solute)}}{\mathrm{Liters(solution)}}$ (1)

The number of moles is calculated by dividing the mass of the sample in grams by the gram formula weight (GFW or molar mass). One GFW is the same as one mole.

Number moles = $\frac{\mathrm{grams(solute)}}{\mathrm{GFW}}$ (2)

For example in a 0.150 M $\mathrm{HNO_3}$ solution, there are 0.150 moles of $\mathrm{HNO_3}$ in one liter of this solution. The following factors may then be used in chemical calculations:

$\frac{\mathrm{0.150molHNO_3}}{\mathrm{1L(solution)}}$ or $\frac{\mathrm{1L(solution)}}{\mathrm{0.150molHNO_3}}$

In a chemical reaction that takes place in solution, the volume and the molarity of one reactant and the molarity of the second reactant can be used together with the stoichiometry of the equation to find the volume of the second reactant needed to react completely with the first reactant.

Titration is a process in which a solution of one reagent, usually the base, is added to an accurately measured volume of another solution, usually the acid, until the reaction is complete. The concentration of one of the reagents is known. From the known concentration and the measured volumes, the concentration of the second solution can be calculated.

In acid-base reactions the end of the reaction or equivalence point is detected by adding a compound that undergoes a color change as it changes from its acid form to its basic form. This compound is called an indicator. An indicator is an organic dye that changes color at a characteristic H^+ ion concentration. A dye can be an indicator if it has an intense color that changes when it gains or loses H^+ ions.

$\mathrm{HIn} + \mathrm{OH^-} \rightarrow \mathrm{In^-} + H_2O$ (3)

The change of an indicator dye from Color A to Color B depends upon the concentration of H^+ (or $\mathrm{OH^-}$) ions. Care must be taken in selecting an indicator to be sure that the color change (endpoint) occurs at the H^+ ion concentration that corresponds to the equivalence point. Phenolphthalein, methyl red, methyl orange, and litmus are examples of indicators.

A primary standard is usually a solid reactant that:

(1) is available in a high purity form

(2) does not change chemically when stored or exposed to air

(3) has a high formula weight to minimize errors in weighing

(4) is soluble in the solvent being used.

Sodium carbonate, $\mathrm{Na_2CO_3}$, is commonly used as a primary standard base for standardizing acids, while potassium acid phthalate (KHP), $\mathrm{KHC_8}H_4O_4$, and oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\mathrm{H_2}O$, are primary standard acids used for standardizing bases.

$\mathrm{Na_2CO_3}(s) + \mathrm{2HCl} \rightarrow H_2O + \mathrm{CO_2} + \mathrm{2NaCl}$ (4)

$\mathrm{KHC_8}H_4O_4(s) + \mathrm{NaOH} \rightarrow \mathrm{KNaC_8}H_4O_4 + H_2O$ (5)

$(\mathrm{COOH})_2 \cdot 2\mathrm{H_2}O(s) + \mathrm{2NaOH} \rightarrow \mathrm{Na_2(COO)_2} + 4\mathrm{H_2}O$ (6)

The dry solid is carefully weighed on an analytical balance and then diluted in a volumetric flask to give a known molarity. The molarity of an acid or base is determined by titrating a measured volume of the acid or base with the primary standard. Then these acid or base solutions can in turn be used to determine the molarity of another acid or base (this is the case with the standardized solutions of NaOH and HCl used in this experiment).

In the example below a known amount of KHP will be titrated with a solution of NaOH to determine the NaOH solution concentration.

EXAMPLE: If 0.8168 g of KHP requires 39.35 mL of NaOH to reach the endpoint in a titration, what is the molarity of the NaOH? (1 mol KHP = 204.2 g)
Equation:

$$\mathrm{0.8168gKHP} \times \left(\frac{\mathrm{1molKHP}}{\mathrm{204.2gKHP}}\right)\left(\frac{\mathrm{1molNaOH}}{\mathrm{1molKHP}}\right)\left(\frac{1}{\mathrm{39.35mLNaOH}}\right)\left(\frac{\mathrm{1000mL}}{\mathrm{1L}}\right) = 0.1016\mathrm{mol}/L = 0.101$$

Notes on titration method:

1. Clean the buret until it drains smoothly.

2. Make sure the stopcock doesn't leak. The level should hold for ~3 minutes.

3. Remove air bubbles from buret tip before beginning. Rapid spurts usually work.

4. Rinse the buret two or three times with 5 mL portions of titrant (the solution you will use to titrate). Hold it horizontal and rotate to rinse.

5. Don't forget to record the initial reading. It does not need to be 0.00 mL.

6. Use a reading card to find the bottom of the meniscus.

7. Always read and record buret volumes to 0.01 mL.

8. Remember that the buret scale reads down, not up.

9. Put white paper under the flask to see color change easily.

10. Swirl the flask with one hand while turning the stopcock with the other or use stir bar and stir plate.

11. Add titrant slowly near the endpoint. Color that dissipates can be seen when getting close to endpoint.

12. Drops can be "split" by quickly turning the stopcock through the open position.

13. Near the endpoint use deionized water from wash bottle to rinse the flask walls from any splashed drops (adding water does not affect number of moles you have).

14. Don't drain buret below 25 mL (You won’t be able to determine final volume accurately). If necessary, read the buret level, refill, read the level, and continue.

Calculation Clarification

Amount neutralized by antacid 25ml of HCLThe amount of HCl that was neutralized by the fragment of the whole tablet, was only neutralized in part, this is where the titration comes in, the solution was still acidic, even after the dissolved antacid fragment, so the volume of NaOH used to finally cause the change in color is equal to the excess of HCl that was in the solution of HCl + water + antacid. So the number of moles of NaOH that was used is equal to the number of moles of HCl that was neutralized by the NaOH. So we DO use the formula in the procedure, so in the report form, where it had asked for the number of moles of HCl neutralized by the antacid:
Equation:

$$n_{\mathrm{HCl neutralized by Antacid}} = n_{\mathrm{HCl added}} - n_{\mathrm{HCl excess}}$$

So then, this would be the 2.5×10^{-3} mol HCl – the excess which is calculated by converting the volume of NaOH used into moles, this number of moles then equals the number of moles oh HCl.

Volume NaOH titratedvolume excess HCl = volume titration of NaOH

Acid and Bases to Buffers

Acids and Bases to Buffers

Objective

- To reinforce the importance of titration as an analytical tool.
- To graphically verify the number of donated protons per molecule of phosphoric acid.
- To prepare a phosphate buffer and realize the importance of buffers in our everyday life.

Grading

- Pre-Lab (10%)
- Lab Report Form (80%)
- TA Points (10%)

Background Information

Phosphoric acid (H_3PO_4) is a chemical that is commonly found in everyday products such as soft drinks and cleaning agents. It is called a *polyprotic* acid because it can donate more than one proton (H^+ ion) per phosphoric acid molecule. The released protons combine with water to form hydronium ions (H_3O^+).

Phosphoric acid releases its protons in a step-wise manner:

$H_3PO_4 + H_2O$ $H_3O^+ + H_2PO$ $K_{a1} = 7.5$ ´10^{-3} (1)

$H_2PO_4^- + H_2O$ $H_3O^+ + HPO$ $K_{a2} = 6.2$´10^{-8} (2)

$HPO + H_2O$ $H_3O^+ + PO$ $K_{a3} = 4.2$´10^{-13} (3)

For example, reaction (2) will not occur until reaction (1) is complete.

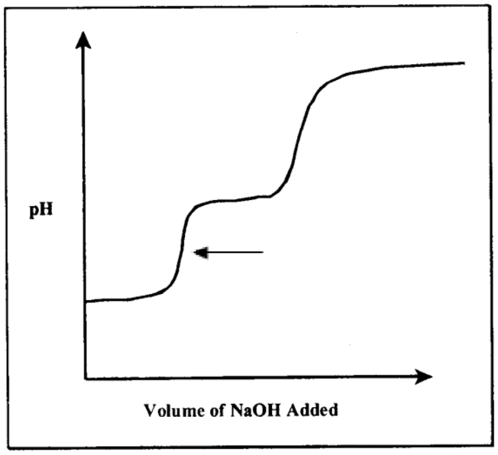
The K_a values listed after each reaction are called acid ionization constants. They indicate the relative ease with which each reaction occurs. A small K_a value shows that a reaction does not occur easily. The K_a value for phosphoric acid’s second donated proton is much smaller than for the first donated proton, while the third K_a is five orders of magnitude smaller than the second.

To determine the amount of acid in an unknown sample, you will need to add a known amount of base until the acid and base are neutralized. This technique is known as *titration*, and it is widely used in chemistry and other natural sciences.

During a titration, the pH of the solution is constantly monitored while the known acid or base (called the titrant) is slowly added to the unknown solution. The pH of the unknown solution will stay fairly constant until the moles of titrant added equals the moles of unknown acid or base. When the moles of acid and base are the same, further additions of titrant will cause a dramatic change in pH until the pH eventually stabilizes. A graph of pH versus added titrant is called a *titration curve*, and the point at which the pH changes drastically is called the *equivalence point*.

The titration curve for a polyprotic acid will have more than one equivalence point. As the added base completely removes each proton from the acid, the pH will jump significantly. Figure 1 shows the titration curve for ascorbic acid, a polyprotic acid also known as Vitamin C:

Figure 1. Titration curve for ascorbic acid.



2nd equiv.point

1st equiv.point

By graphing the pH versus volume of base added during an acid-base titration, you can easily see the successive ionization steps taking place. To find the concentration of a polyprotic acid, the volume of base required to reach the first equivalence point is needed. The half-equivalence points on this graph can also be used to obtain the K_a value of each successive ionization.

In the third part of the lab, you will be making a buffer solution. Buffers are important in everyday life because they regulate the pH in our blood, keeping the pH between 7.35 and 7.45; if pH values for our blood go outside this range, death can result. A buffer is composed of a weak acid and its conjugate base (or a weak base and its conjugate acid). When a strong acid or base is added to a buffer, one of the species will react to maintain the pH within a small range.

To determine the amount of conjugate acid and base needed to make a buffer of a certain pH, the Henderson-Hasselbach must be employed.

—— (4)

With a given pH and known pK_a, the solution of the Henderson-Hasselbach equation gives the logarithm of a ratio which can be solved by performing the antilogarithm of pH/pK_a.

—— (5)

Experimental Procedure

Materials Required

- pH electrode and pH 7 buffer for calibration
- burette
- 250 mL beaker
- magnetic stirrer
- 0.4 M and 0.1 M NaOH
- 0.2 M phosphoric acid
- buffer solutions (pH 4 and pH 7)

Part I. Demo During PreLab Lecture: Drink Anyone?

1. Six wine glasses are filled with the same “mystery” liquid.
2. Each glass takes on a different color of the rainbow, despite the fact that the same liquid was added to each.

Part II. Titration of Phosphoric Acid

1. Obtain a pH probe and connect it to pH/mV 1 on the Microlab interface. Open the MicroLab program and select “Microlab Experiment.” Choose “Add Sensor.” This will bring up a window where you need to select “pH /D.O.”, click on the appropriate port of the interface, and choose “pH” out of the two options below. To calibrate the pH probe, click “next.”

2. Take a sample of two buffer pH standards at pH 4.00 and 7.00. Calibrate the pH probe with these two solutions. This is done by selecting “Add Calibration Point” and entering the correct pH value noted on the bottle. **Note that the pH probe should always be rinsed with deionized water and carefully patted dry before being inserted into a solution so as to avoid cross contamination.** A large waste beaker is useful to have for rinsing. After the two points are entered, select linear calibration, and save the calibration data.
3. In a dry beaker, obtain 30 mL of a 0.2 M phosphoric acid solution. Use a graduated cylinder to add 50 mL of deionized water to a 250 mL beaker. Rinse your 10 mL volumetric pipette with the phosphoric acid solution and pipette 10 mL of the acid into the water. Rinse and fill your 25 mL burette with 0.4 M NaOH. The initial burette reading should be 0 mL. Remember to clear the air out of the tip of the burette.
4. Place the beaker on the magnetic stirrer and add a stir bar. Position the burette ready for titration. Insert the pH probe. Turn on the magnetic stirrer and adjust the stirring rate to moderate speed (without allowing the stir bar to splash or hit the probe).
5. On the Microlab main screen choose “Add Sensor” and select “Keyboard” under the sensor drop box. Click “Next.” This will bring up a prompt in which you should enter “KBD” in the top box and “mL” in the bottom “units” box, and then hit “Finish.”
6. Drag the keyboard sensor from the top left of the screen to “Data Source 1” on the x-axis of the graph. Drag the pH sensor to “Data Source 2” on the y-axis of the graph. Drag the pH sensor to the box in the bottom right corner.
7. Click “Start.” Enter your starting volume, 0 mL, in the window that appears, and hit enter. The window will not disappear. Slowly add a small volume of NaOH to the beaker, approximately 0.5 mL, enter the reading on your burette into the box, and hit enter. Repeat this process until both peaks have been observed and the pH has stabilized.
8. To save your data, choose “export data” under File, and select “comma separated value.” For help with plotting the data and derivative of the data see the “Data Analysis” section below.

Part III. Buffers (Use the same MicroLab program)

1. Using equations (4 and 5), calculate the ratio of concentrations of and to produce 100 mL of buffer solution with pH = 6.91. Show your calculations to your TA before proceeding.
2. Prepare your buffer solution from 0.1 M and 0.1 M solutions.
3. Insert the pH probe in your buffer solution and wait until the reading becomes stable and write down the value in your report form. Don’t worry if the pH reading isn’t exactly 6.91. The important thing is that there isn’t a drastic change in pH upon addition of acid or base.
4. Pour 50 mL of the buffer solution into another beaker so that you have two beakers each with 50 mL of your buffer solution.
5. Add 1 mL of 0.1 M NaOH to the first beaker and mix the solution with a glass rod. Wait until the pH reading becomes stable and write down the value in your report form. If the pH of your buffer solution changes by more than 0.3 pH units, you will need to redo the calculations and re-prepare the buffer solution in order to get an acceptable result.
6. Add 1 mL of 0.1 M HCl to the second beaker and mix the solution with the glass rod. Insert the pH probe into the second beaker. Wait until the pH reading becomes stable and write down the value in your lab report form. If the pH of your buffer solution changes by more than 0.3 pH units, you will need to redo the calculations and re-prepare the buffer solution in order to get an acceptable result.

Data Analysis

Two plots need to be made from the data taken in Part II. One plot, pH vs. volume of NaOH, can be made directly from the data that is initially present. The data needs to be further analyzed to make the plot of the first derivative. This plot should be (pH / vol NaOH) vs. volume of NaOH. Remember to include a title and axis labels.

Electrochemistry/Alchemy: Molar Mass of Cu and Turning Cu into Au

Electrochemistry/Alchemy:

Molar Mass of Cu and Turning Cu into Au

Objectives

- To learn Faraday’s two laws of electrolysis
- To relate an electric current to the passage of an amount of electric charge
- To discuss electrolysis in molten salts and in aqueous solutions
- To determine the molar mass of copper by electrodeposition from an aqueous solution
- To copper into gold (please bring to lab with you a penny that is pre-1982)

Grading

You grade will be determined according to the following:

- Pre-lab (10%)
- Report Form (80%)
- TA evaluation of lab procedure (10%) – including bringing a pre-1982 penny to lab

Before Coming to Lab …

- Read and complete the pre-lab
- Read the background information
- Read and be familiar with the Lab Instructions
- Find a pre-1982 penny and bring it with you to lab

Introduction

Electrochemistry describes the interaction between electrical energy and chemical processes. Electricity continues to intrigue us, as it has since people first observed the sky shattered by bolts of lightning. Electrochemistry is of great practical value to contemporary living. Consider the number of batteries used for powering the many portable items of pleasure and need – everything from cassette recorders to hearing aids, from calculators to pacemakers. Pure metals are produced from natural ores, inorganic and organic compounds are synthesized, metal surfaces are plated with other metals or coated with paint to enhance their value and utility – all through electrochemistry.

Electricity is a moving stream of electrical charges. This flow, or electric current, can occur as electrons moving through a wire or as ions flowing through an aqueous solution. If the electrons lost and gained in a spontaneous reaction can flow through a wire on their pathway from the substance oxidized to the substance reduced, the energy of the reaction is released as electrical energy. Conversely, a non-spontaneous redox reaction can be driven forward by the introduction into the system of electrical energy from another source. Any device in which either process can occur is called an electrochemical cell.

There are two types of electrochemical cells. The first type generates electrical energy from a spontaneous redox reaction. These are called voltaic or galvanic cells, common household batteries are classic examples. An Italian physicist, Allesandro Volta in 1800 explained that electricity is generated by the connection of two dissimilar metals separated by any moist body (not necessarily organic). A simple voltaic cell, similar to that made by Volta, can be assembled using twelve pennies and twelve nickels (construct a column of alternating pennies and nickels with each coin separated by disk-size pieces of wet filter paper soaked in salt water).

In the second type of electrochemical cell, called an electrolytic cell, a non-spontaneous redox reaction is caused by the addition of electrical energy from a direct current source such as a generator or a storage battery. The process of generating a non-spontaneous redox reaction by means of electrical energy is called electrolysis.

Electrolysis can be used for purifying a metal through the electrolytic dissolution of an impure anode and the subsequent re-crystallization of the pure metal on the cathode. The impurities are left behind in solution. Copper is refined commercially by this electrolytic technique.

Electrolysis is often used for electroplating a metal to another material acting as the cathode. The other material must also be electrically conducting. Non-conducting materials, such as leaves, can also be plated by first being painted with a metallic conductive paint. Silver plating can be done with a silver anode and the object to be plated as the cathode.

Electrolytic reduction (cathodic reduction) has developed into a useful technique for the restoration of artifacts such as corroded nails and encrusted silver. In the case of silver, the degradation is usually due to the surface formation of insoluble (black) silver sulfide (Ag_2S). The artifact (a silver coin, for example) is attached to the negative electrode of the electrolysis cell. The Ag^+ ions of the silver sulfide pick up electrons and are converted back to metallic silver:

$$\mathrm{Ag}_2S(s) + 2\mathrm{e}^- \rightarrow 2\mathrm{Ag}(s) + S^{2-}(\mathrm{aq})$$

The sulfide ions are swept away by the water and the surface of the object is restored.

In this experiment, you will electroplate copper quantitatively to a copper cathode (the anode is also composed of copper). The current is measured over an interval of approximately one hour so that the amount of charge passing through the cell is known. The molar mass of copper is calculated from its equivalent mass using Faraday’s second law. In the second part of the experiment, you will use turn copper into gold!

Background Information

In the 1830s, Michael Faraday published his experiments using the recently discovered voltaic column to decompose substances through the use of electric current. Electrolysis is an oxidation-reduction process involving a conversion of electrical energy to chemical energy. The electrolytic cell is a galvanic cell operating in reverse. The automobile battery is acts as a collection of galvanic cells when delivering electric current, but acts as a collection of electrolytic cells when being recharged.

Faraday first described the quantitative relationships between the amount of electric charge (number of electrons) that has passed through an electrolytic cell and the amount of materials that have formed at the electrodes. These are summarized as Faraday's Laws of Electrolysis:

1. The mass of substance reacting at an electrode is directly proportional to the total amount of electric charge that has passed through the cell.
2. The masses of the substances reacting at the electrodes are in direct ratio to their equivalent masses. The equivalent mass of a reacting substance is defined as its mass that reacts with one mole of electrons in the oxidation or reduction process. In the case of sodium and chlorine, the equivalent masses of the sodium and chlorine are equal to their molar masses; the equivalent mass of copper is equal to its molar mass divided by two. The second law is a consequence of the stoichiometry of the balanced half-reactions.

Through exhaustive experimentation, the charge of a single electron has been determined to be 1.602×10^{-19} coulombs (C). (The coulomb charge unit – defined as useful for much larger charged objects – is inconvenient for expressing such a small charge, so other electrical charge units are commonly used.) One mole of electrons has a total charge calculated to be 96,485 C; this quality is defined as faraday (F):

$$1 \text{ F} = 96{,}485 \text{ C/mol e}^-$$

Electric currents (l) are measured in amperes (A), amps for short, and defined in terms

I = Q/t

1 A = 1 C/s

For example, a constant current of .600 A (milliamperes) over a period of 2.00×10^2 seconds represents

$$Q = I \times 5 = 0.600\ \text{A} \times 200\text{s} = 0.600\ \text{C/s} \times 200\text{s} = 120\ \text{C}$$

a movement of 120 coulombs. The number of moles of electrons (n) transported during the time interval is

$$\text{n} = \frac{120\ \text{C}}{96{,}485\ \text{C/mole}^{-1}}$$

$$= 1.24 \times 10^{-2}\text{mol e}^{-1}$$

Time intervals measured in minutes and hours must be converted to seconds in such calculations. Another useful equation in Electrochemistry is Ohm's Law, where: V = I R where V is the potential difference in volts, I is the current in amperes and R is a constant, measured in ohms, called the resistance.

Experimental Procedure

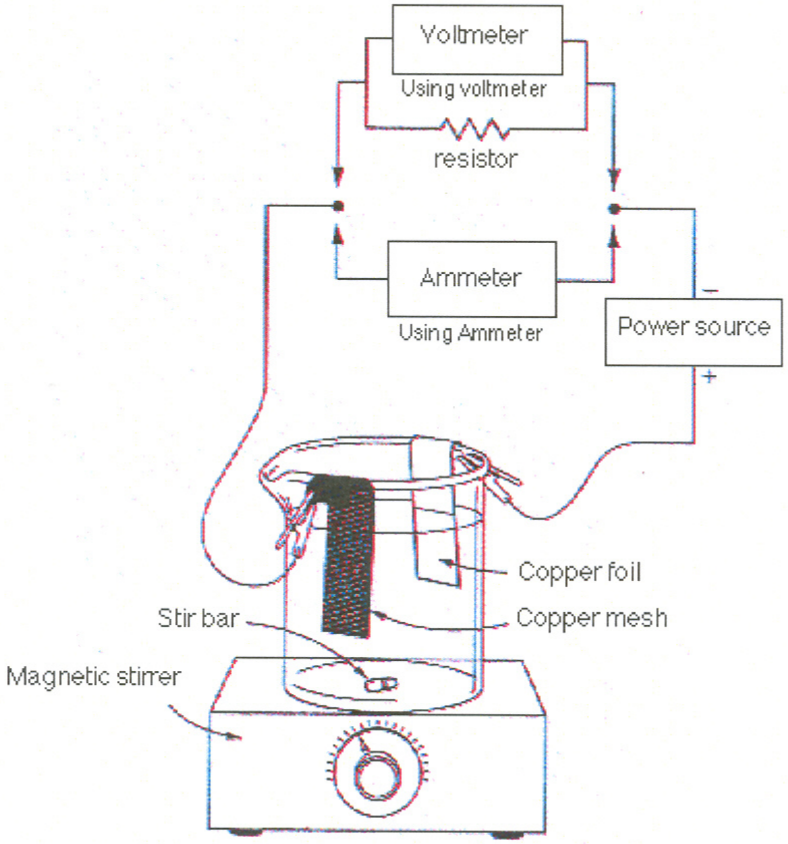


Figure 1

CAUTION WEAR EYE PROTECTION!

CAUTION The 6 M nitric acid used in the next step will burn and stain the skin as well as damage clothing. In case of skin or clothing contact, wash the area immediately with large amounts of water.

1. Obtain a piece of copper foil (about $2\ \mathrm{cm} \times 8\ \mathrm{cm}$). Holding the foil with tweezers or tongs, dip it into 6 M nitric acid several times until its surface is bright and shiny. Do not allow tweezers or tongs to touch the acid solution. Rinse the foil in de-ionized water and set it aside. This is the anode. Set the nitric acid aside to use in the electroplating exercise.
2. Obtain a piece of copper mesh (about $5\ \mathrm{cm} \times 8\ \mathrm{cm}$) and remove any loose pieces of copper. Clean and rinse it as in step 1. Place the copper mesh on a watch glass in the drying oven. Be careful not to touch the cleaned surfaces. This is the cathode.

3. Add 350 mL 1.0 M KNO_3 solution to a 400 mL beaker.

CAUTION The copper sulfate used in the next step is toxic. Avoid skin contact

1. To this solution, add about 5 mL of 1 M $H_2\mathrm{SO}_4$ and 10 g of $\mathrm{CuSO}_4 5\mathrm{H}_2 O$. Stir until the copper sulfate pentahydrate is fully dissolved.
2. Assemble the apparatus shown in Figure 1, but leave the copper mesh electrode in the oven. Add a magnetic stirring bar to the beaker. If necessary, add additional 1.0 M KNO_3 to bring solution level in the beaker within 2 cm of the rim. You will either measure the electric directly with an ammeter in series with the electrolytic cell or you will measure the current indirectly by measuring the voltage across a resistor of known value (about 10 ohms).
3. Remove the copper mesh electrode from the oven, let it cool, and determine its mass to the nearest milligram.
4. Attach the copper mesh electrode to the negative terminal of your power supply using an alligator clip. Turn on the magnetic stirrer.
5. Turn on the low voltage power supply and adjust the current until about 140 mA are flowing through the cell. Record the time and current.
6. Record the time and current every five minutes for an hour.
7. After the last reading, gently remove the cathode from the solution while yet attached to the power supply. After the copper mesh has cleared the solution, remove the wire and turn off the power supply.
8. Gently dip-rinse the copper mesh electrode several times in a beaker of deionized water, and place it on a watch glass in the drying oven.
9. When dry, remove the electrode from the oven and let it cool. Reweigh the mesh electrode.
10. Remove the magnetic stirring bar from your beaker and dispose of the solution in the sink.

Alchemy: Copper into Gold

Place your pre-1982 copper penny in an evaporating dish and heat with a mixture that first turns it silver, then suddenly turns it gold when the penny is then heated on a hot plate.

Caution: Wear safety goggles and gloves, do the reaction in the fume hood with the sash down. Note step 10: special disposal

1. Place approximately 5 g of zinc in an evaporating dish.
2. Add enough NaOH solution to cover the zinc and fill the dish about one-third.
3. Place the dish on a hot plate and heat until the solution is near boiling.
4. Prepare a copper penny (pre-1982) by cleaning it thoroughly with a light abrasive (steel wool pads work well).
5. Using crucible tongs or tweezers, place the cleaned penny in the mixture in the dish.
6. Leave the penny in the dish for 3-4 min. You will be able to tell when the silver coating is complete.
7. Remove the penny, rinse it, and blot dry with paper towels. (Do not rub.) Remove particles of zinc.
8. Using crucible tongs or tweezers, place the coated penny on the hot plate. The gold color appears immediately.
9. When the gold color forms, remove the coin, rinse it, and dry it with paper towels.
10. Special disposal procedures: Do not discard the waste zinc in the trash container. When zinc dries, it forms a powder that may spontaneously ignite. Rinse the NaOH-zinc mixture several times with water. Then add the solid to a beaker that contains 200 mL of 1 M $H_2\mathrm{SO}_4$. When all of the solid dissolves, flush the zinc sulfate solution down the drain.

Example of the calculation of Molar Mass:

1. Graph the electric current (in amps) on the y-axis against time (in seconds) on the x-axis. The total charge that passed through the electrolysis cell is given by the area beneath this curve. If the current is constant, this area is:

$$Q = \text{area} = I \times t$$

Calculate this charge in coulombs.

1. Convert the coulombs of charge to mol electrons:

N =

$$\frac{Q(C)}{96{,}485C/mol}$$

The equation for the reduction half-reaction responsible for the plating at the cathode is

$$\mathrm{Cu}^{2+}(\mathrm{aq}) + 2\mathrm{e}^{-} \rightarrow \mathrm{Cu}(s)$$

Use the mol ratios of the preceding balanced equation to calculate the number of moles of Cu plated out:

$$\frac{n(Cu)}{n} = \frac{1}{2}$$

$$n(\mathrm{Cu}) = \mathrm{n}/2$$

1. Use the initial and final weighings of the copper mesh electrode to calculate the mass of copper plated out:

m(Cu) = m(final) – m(initial)

1. Calculate the molar mass (M) of copper:

M =

$$\frac{m(Cu)}{n}$$

Electrochemistry Pre-lab Exercise

Hopefully here for the Pre-Lab

Note: In preparing this report you are free to use references and consult with others. However, you may not copy from other students' work (including your laboratory partner) or misrepresent your own data (see honor code).

Name(Print then sign):
____

Lab Day: ___________________Section:
________TA__________________________

This assignment must be completed individually and turned in to your TA at the beginning of lab. You will not be allowed to begin the lab until you have completed this assignment.

1. Write a balanced chemical equation for the electrolysis of molten potassium iodide (KI).

2. An electric current of 0.211 mA passes through an electrolytic cell for 2.00 min. How many moles of electrons have passed through the cell?

3. A voltage drop of 3.412 V is measured across a resistance of 10.51 ohms. How much current is flowing through the resistor?

4. Why is the anode not weighed before electrolysis begins?

Report Form: Electrochemistry

Hopefully here for the Report Form

Note: In preparing this report you are free to use references and consult with others. However, you may not copy from other students’ work (including your laboratory partner) or misrepresent your own data (see honor code).

Name(Print then sign): ____

Lab Day: ____________________Section: _________TA____________________________

Initial mass of cathode ____________________g

Final mass of cathode ____________________g

Mass of copper plated out ____________________g

Time (min)	Voltage (V)	Current (A)
5		
10		
15		
20		
25		
30		
35		
40		
45		
50		
55		
60		

Show calculations for full credit!

Average Current = (A)

Total charge through cell _______________C

Number of moles e^- through cell _______________mol

Molar mass of copper _______________g/mol

Questions:

1. What is oxidized and what is reduced when electroplating copper?

2. Write the half reactions that occur at the anode and electrode.

3. Why is it important not to touch the cleaned cathode?

4. What is the purpose of KNO_3 in this experiment?

5. How would your results for the molar mass of copper be affected if hydrogen gas were also observed at the cathode?

6. What part of this procedure limits the accuracy of the molar mass determination?

Alchemy - Copper into gold

1. Is this reaction an oxidation-reduction reaction?

1. Why did the penny turn "silver"?

1. Why did it turn "gold"?

1. Why did we heat the penny to turn it "gold"?

Polymers

Macromolecules: Natural and Synthetic Polymers

Objectives

In this laboratory you will become familiar with the classifications of polymers by synthesizing and examining several of the following:

- a cross-linked condensation copolymer (Glyptal ^{TM} resin)
- a branched addition polymer (polymethylmethacrylate)
- a loosely cross-linked silicon-based condensation polymer (a polymethylsiloxane)
- a cross-linked polyvinyl alcohol

Additional information about polymers can be found in Chapter 12 of your textbook.

Grading

Your grade will consist of the following:

- Pre-lab (10%)
- Correctness and thoroughness of your observations and the answers to the questions on the report form (80%)
- TA evaluation of lab procedure (10%)

Before Coming to Lab . . .

- Complete the pre-lab exercise
- Read the introduction and any related materials provided to you

NOTE: If you wear contact lenses, for this week’s lab, you may prefer to wear your prescription glasses.

Introduction

Approximately 50% of the industrial chemists in the United States work in some area of polymer chemistry, a fact that illustrates just how important polymers are to our economy and standard of living. These polymers are essential to the production of goods ranging from toys to roofing materials. So what exactly are polymers? Polymers are substances composed of extremely large molecules termed macromolecules, with molecular masses ranging from 10^4 to 10^8 amu. Macromolecules consist of many smaller molecular units, monomers, joined together through covalent bonds. The molar mass of the polymer is quoted as an average molar mass.

Both natural and synthetic polymers are ubiquitous in our lives: elastomers (polymers with elastic, rubber-like properties), plastics (the first plastic was used in 1843 to make buttons), textile fibers, resins, and adhesives. The more common polymers include acrylics, alkyds, cellulosics, epoxy resins, phenolics, polycarbonates, polyamides, polyesters, polyfluorocarbons, polyolefins, polystyrenes, silicones, and vinyl plastics, to name but a few.

Naturally occurring macromolecules are derived from living things: wood, wool, paper, cotton, starch, silk, rubber and have provided us for centuries with materials for clothing, food, and housing. Starch, glycogen, and cellulose are all polymeric versions of the monomer glucose. Again, we see that minor structural variations create chemicals with very different properties. Proteins are macromolecules composed of monomeric units of alpha amino acids; nucleic acids are composed of subunits (nucleotides) containing a nitrogeneous base, sugar and phosphate groups. Natural rubber is a latex exudate of certain trees and composed of monomers called isoprene units. The usefulness of latex was first discovered by Lord Mackintosh in Malaysia in the last century and provided the foundation of his waterproof rainwear empire.

The temptation to improve upon nature has always been great and has rarely been resisted. When scientists linked the special properties of these substances (physical properties such as tensile strength and flexibility) to the sizes of their molecules the next logical step involved chemical modifications of naturally occurring polymers.

Synthetic celluloid derives from natural cellulose and stems from an accident that Christian Schoenbein, a chemistry professor had in 1846. The age of plastic had begun, although the interest in cellulose nitrate was initially more for their explosive properties. When cellulose (from wood chips or fiber) is treated with a mixture of nitric acid, camphor, and alcohol, the resultant product is called Celluloid $^{\text{TM}}$ and bears very little resemblance to the starting material. Celluloid $^{\text{TM}}$ possess the ability to be molded into hard, smooth billiard balls (replacing the original, very expensive ivory balls) and into thin sheets for making movie pictures. Celluloid $^{\text{TM}}$ is highly flammable and today has been replaced by greatly improved synthetic polymers such as bakelite discovered in 1907 by the Belgian-American Chemist, Leo H. Baekeland.

When cellulose is treated with sodium hydroxide and carbon disulfide (CS_2), cellulose xanthate is formed. A viscous (thick) solution of cellulose xanthate, forced through fine holes into dilute sulfuric acid, regenerates the cellulose as fine, continuous, cylindrical threads called rayon. If the solution is forced instead through a narrow slit, a thin transparent film or sheet is obtained called cellophane.

Classification of Polymers: Thermoplasts versus Thermosetting

Polymers generally are classified into two broad groups in accordance with their behavior upon heating. Polymers that can be repeatedly melted and solidified (without damage) are said to be thermoplasts; those that solidify once but will not melt again without damage are said to be thermosets. Technically, only thermoplasts are true plastics, even though the term "plastic" is commonly applied to all synthetic polymers.

The thermoplastic substance contains long, thin molecules which form tangled chains and is rigid at lower temperatures but gradually softens upon the application of heat, after it passes a characteristic temperature known as its glass transition temperature (Tg). Below Tg, the substance is brittle, having the characteristic properties of a glass; above Tg, the substance becomes flexible and soft. Chewing gum is a thermoplast that becomes extremely brittle when the outside temperatures drop below its glass transition temperature - this is a useful property to use in order to remove chewing gum from your clothes. Once warmed above Tg, however, the gum quickly softens and regains its flexibility. Some thermoplasts, such as polystyrene, melt before reaching their glass transition temperatures and remain rigid materials up to their melting points. Thermoplastic polymers are used frequently for injection molding of such items as food storage containers and toys that are not exposed to high temperatures. Additionally, thermoplastic polymers can be molded, pressed and extruded.

Thermosetting substances contain large, cross-linked molecules that are rigid at lower temperatures, and undergo irreversible chemical and physical changes (including decomposition) upon heating. Such substances remain solids at higher temperatures than thermoplastic materials, and they do not melt. Thermosets are often employed in high-temperature environments, such as for electrical insulation in electric motors and gasoline engines.

Thermoplastic polymers are composed of small monomers covalently bonded end-to-end in a long chain but without covalent bonds joining adjacent chains. Such macromolecules constitute the linear polymers. Shorter side groups attached to the long chains at periodic intervals, cause the polymers to be termed branched polymers. The chains, having average molecular masses up to one million amu, may be independent of each other (as in polyethylene) or loosely lined through hydrogen bonding (as in nylon). If the long chains are linked by covalent bonds, the polymeric network becomes two- or three-dimensional, resulting in an infusible (nonmelting) and insoluble material. Such macromolecules make up the cross-linked polymers, and are found in thermosetting materials. Polymers of all types in which the long chains are produced by joining two or more different kinds of monomers are termed copolymers.

Addition and Condensation Polymers

The process by which the polymerization reaction occurs permits classification of polymers into two categories: addition and condensation polymers. Addition polymers are those in which the monomers join at unsaturated carbon atoms (coupling occurs using the monomer’s multiple bonds); several are summarized in the Table. During polymerization, the double bonds between the pairs of carbon atoms 'open up' and the carbon atoms of separate ethylene molecules join together to form a molecule of polyethylene. The first polymerization of ethylene was accomplished in 1933 by the use of very high pressure (1000 atm) and oxygen as a catalyst. Nowadays, with the development of the use of powerful catalysts, addition can occur at atmospheric pressure. Polymethyl methacrylate, also called Lucite $^{\text{TM}}$ or Plexiglass $^{\text{TM}}$ (originally developed as an unbreakable substitute for glass in airplane canopies), belongs to this group of addition polymers. The polymerization is initiated by a variety of substances (such as benzoyl peroxide) that can form a free radical with the unsaturated carbon atom. The resulting addition polymer is described as a branched polymer.

The second way to make a polymer is by condensation polymerization. In this process, two compounds with reactive atoms at the end of their molecules react, usually with the release of a small molecular unit such as water or hydrogen chloride. The presence of two or more functional groups in the monomer usually leads to the production of a cross-linked polymer. Glyptal $^{\text{TM}}$ resin, formed by the reaction between phthalic acid and glycerol, is a condensation copolymer, a copolymer since 2 different types of monomers combine to form the chain.

Polyester is formed when the monomers are linked via ester $(-C(=O)-O-\mathrm{CH_2}-)$ bonds. The more reactive phthalic anhydride is often used in place of phthalic acid in this reaction.

Paper is composed of naturally occurring cellulose, the polymeric structural material of plants. The cellulose chains are composed of linear glucose units. Parchment paper is made by cross-linking the linear cellulose polymer to form a sheet-like structure. Adjacent chains are cross-linked by ether $(-\mathrm{CH_2}-O-\mathrm{CH_2}-)$ bonds resulting from dehydration of the alcohol groups (through the use of sulfuric acid as the dehydrating agent). Resulting reactions that form the macromolecules required for polymerization by either addition or condensation processes must be capable of proceeding indefinitely.

By far the most interesting uses of polymers involve replacement of diseased, worn out, or missing parts of the human body including flexible replacements for major blood vessels, replacement valves for hearts, temporary skin, and artificial joints. Artificial ball-and-socket pelvic (hip) joints made of steel (ball) and plastic (socket) are installed at the rate of 25,000 per year. People with crippling arthritis, debilitating coronary and circulatory problems, and burns all benefit from the development of biomedical polymers. Preventive and cosmetic dentistry, as well, benefit from polymers used to seal porous teeth and reconstruct missing enamel.

Linear silicones, or polysiloxanes, are comparatively new polymers based upon silicon-oxygen-silicon linkages. These polymers may be cross-linked to various degrees by additional -Si-O-Si- bonding between adjacent chains:

The R group is generally a hydrocarbon group such as $-\mathrm{CH_3}$ (methyl), $-\mathrm{CH_2CH_3}$ (ethyl), or $(-C_6H_5$ (phenyl). Silicones are stable at much higher temperatures than carbon-based polymers, yet they remain flexible even at exceedingly low temperatures. Among such silicones is Silly Putty $^{\mathrm{TM}}$, the cross-linked polymerization product of dimethyldichlorosilane.

TABLE 1. Addition Polymers

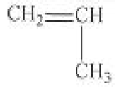
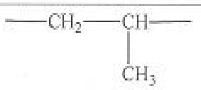
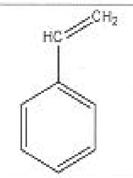
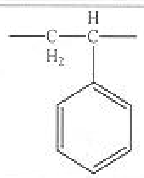
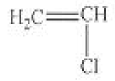
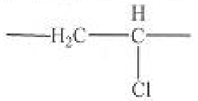
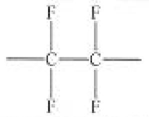
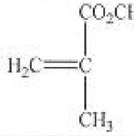
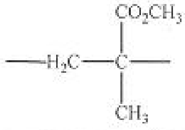
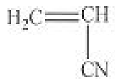
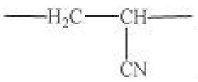
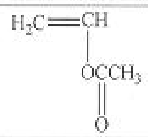
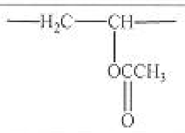
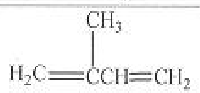
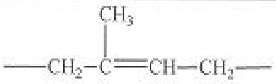
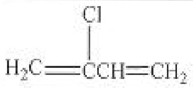
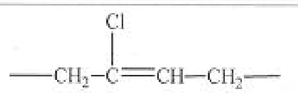
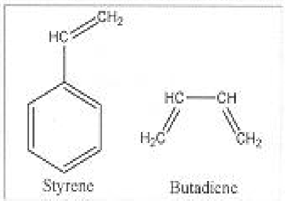
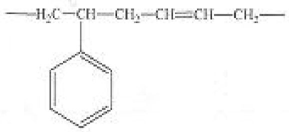
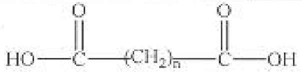
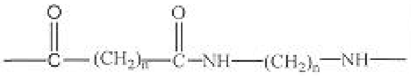
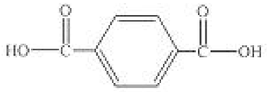
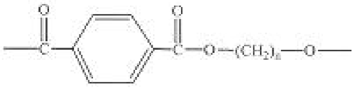
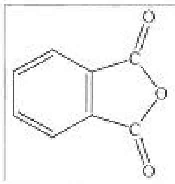
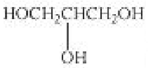
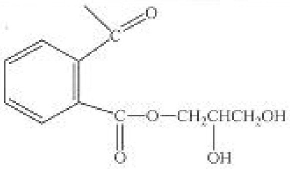
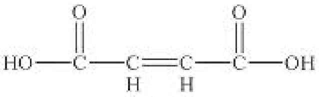
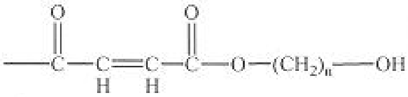
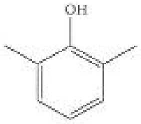
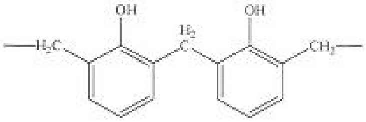
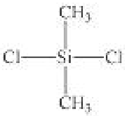
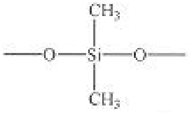
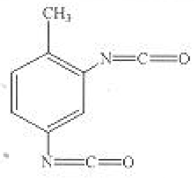
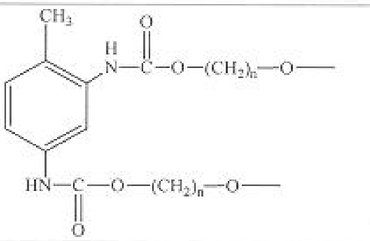
Example	Monomer(s)	Polymer	Use
Polyethylene	$CH_2{=}CH_2$	$-CH_2-CH_2-$	Common polymer: bags, wire insulations, squeeze bottles
Polypropylene	 $\underset{CH_3}{CH_2{=}CH}$	 $-CH_2-\underset{CH_3}{CH}-$	Fibers, indoor-outdoor carpet, bottles, rope
Polystyrene			Styrofoam^{TM}; drinking cups, building insulation, packing materials
Polyvinylchloride **(PVC)**	 $H_2C{=}\underset{Cl}{CH}$	 $-H_2C-\overset{H}{\underset{Cl}{C}}-$	synthetic leathers, clear bottles, floor coverings, phonograph records, water pipes
Polytetrafluoroethylene	$F_2C{=}CF_2$	 $-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$	Teflon^{TM}; nonstick surfaces, chemically resistant films, cookware coatings
Polymethylmethacrylate	 $H_2C{=}\overset{CO_2CH_3}{\underset{CH_3}{C}}$	 $-H_2C-\overset{CO_2CH_3}{\underset{CH_3}{C}}-$	Lucite^{TM}, plexiglass^{TM}; unbreakable glass, latex paints
Polyacrylonitrile	 $H_2C{=}\underset{CN}{CH}$	 $-H_2C-\underset{CN}{CH}-$	Orlon^{TM}, Acrilan^{TM}, Creslan^{TM}; fibers for sweaters, blankets, carpets
Polyvinylacetate **(PVA)**	 $H_2C{=}\underset{\underset{O}{\overset{\Vert}{OCCH_3}}}{CH}$	 $-H_2C-\underset{\underset{O}{\overset{\Vert}{OCCH_3}}}{CH}-$	adhesives, latex paints, chewing gum, textile coatings
natural rubber	 $H_2C{=}\overset{CH_3}{C}CH{=}CH_2$	 $-CH_2-\overset{CH_3}{C}{=}CH-CH_2-$	The polymer is cross-linked with sulfur (vulcanization).
Polychloroprene (neoprene rubber)	 $H_2C{=}\overset{Cl}{C}CH{=}CH_2$	 $-CH_2-\overset{Cl}{C}{=}CH-CH_2-$	cross-linked with zinc oxide; resistant to oil, gasoline
Styrene-Butadiene Rubber **(SBR)**			cross-linked with peroxides; most commonly used for tires, 25% styrene, 75% butadiene

TABLE 2. Condensation Polymers

Example	Monomer(s)	Polymer	Use
Polyamides (nylon)	 $HO-C(=O)-(CH_2)_n-C(=O)-OH$ $H_2N-(CH_2)_n-NH_2$	 $-C(=O)-(CH_2)_n-C(=O)-NH-(CH_2)_n-NH-$	fibers, molded objects
Polyesters	 $HO-(CH_2)_n-OH$		Dacron ™, Mylar ™, Fortrel ™; linear polyesters, fibers, recording tape
Polyesters	  $HOCH_2CH(OH)CH_2OH$		Glyptal ™ resin; crosslinked polyester; paints
Polyesters	 $HO-C(=O)-CH=CH-C(=O)-OH$ $HO-(CH_2)_n-OH$	 $-C(=O)-CH=CH-C(=O)-O-(CH_2)_n-OH$	casting resin; crosslinked with styrene and peroxide: fiberglass, boat resin
Phenol formaldehyde resin	 $O=CH_2$		Bakelite ™; mixed with fillers: molded electrical goods, adhesives, laminates, varnishes
Silicones	 $Cl-Si(CH_3)_2-Cl$ H_2O	 $-O-Si(CH_3)_2-O-$	water-repellant coatings, temperature resistant fluids, rubbers (CH_3SiCl_3 crosslinks in water)
Polyurethanes	 $HO-(CH_2)_n-OH$		rigid and flexible foams, fibers

Experimental Procedure

A. Polymethylmethacrylate (addition polymer)

CAUTION: Benzoyl peroxide can explode when heated; do not exceed the stated amount of benzoyl peroxide and be sure to wear eye protection. Avoid breathing the fumes generated during step 8 – the monomeric methyl methacrylate is toxic.

- Half-fill a 400 mL beaker with deionized water and set it aside. Begin to heat an hot plate.
- Transfer 5.0 mL water into a clean 6-inch (15 cm) test tube, and make a 5.0 mL calibration mark on the tube with a piece of tape or a glass-marking pencil.
- Drain and thoroughly dry the test tube.
- Carefully fill the dry test tube up to the 5.0 mL calibration mark with methylmethacrylate. Add 2-3 drops of food coloring to the solution.
- Add about 20 mg benzoyl peroxide to the test tube using a small wooden spatula. This amount is approximately equal in volume to that of a pea.
- Prop the test tube up in the 400 mL beaker (beaker containing deionized water).
- Stir the contents of the test tube with a chopstick until the benzoyl peroxide is dissolved. Remember to wash and return the chopstick when you are finished.
- Continue to heat the test tube in the water bath; do not stir until the contents start to thicken, remove from the heat before the mixture starts to foam. This may take up to 45 minutes so move onto the next synthesis.
- Remove the test tube from the water bath and slowly pour the thick, warm liquid into the plastic cup that is half filled with warm water from the tap.
- Examine the film that forms on the surface of the water, and describe its appearance. This may need to sit on water for a while.
- If nothing is observed, stir the solution and describe any observations.

B. Synthesis of Nylon (to be performed in the hood by Dr McHale): Two liquids are mixed in a small beaker and nylon is formed at their interface.

The nylon is pulled from the beaker; a continuous thread 10-15 ft long can be formed. CAUTION: Wear gloves while performing this experiment; do not touch the nylon with your bare hands until it has been rinsed thoroughly with water.

1. Solutions A and B have been prepared for you:

- Solution A: A 0.5 M basic solution of hexamethylenediamine (or 2,6-diaminohexane, $H-\mathrm{NH}(\mathrm{CH}_2)_6\mathrm{NH}-H$) was prepared as follows: Weigh 5.81 g in a large beaker and dilute to 100 mL with 0.5 M NaOH solution (20 g of NaOH per liter). Warm the solid until it melts. Wear gloves; hexamethylenediamine is absorbed through the skin.
- Solution B: Adipoyl chloride $(\mathrm{Cl}-(C=O)-(\mathrm{CH}_2)_4^-(C=O)-\mathrm{Cl})$, 0.25 M: Weigh 4.58 g and dilute to 100 mL with cyclohexane.
- Place 5 mL of solution A in a small beaker. Place 5 mL of solution B in a second beaker
- Slowly add solution A to solution B by gently pouring it down the side of the beaker. Do not stir or mix. Solution A should form a separate layer on top of solution B.
- A film will form at the interface of the two solutions.
- Carefully hook the film with a bent paper clip and pull the film from the beaker.
- Continue pulling until the solutions are exhausted.
- If you want to keep the nylon, rinse it several times with water until it is free of all traces of amine.

C. Glyptal $^{\mathrm{TM}}$ Resin (linear condensation copolymer): A small aluminum dish is used to mold the polymer. A coin, favorite small stone, or small flower may be placed on the bottom of the mold if you wish to make a souvenir of this experiment. This will harden several hours after your lab has finished.

CAUTION: Use care when heating any of the solutions – if the solutions come in contact with your skin, severe burns could result.

1. In a large test tube, mix 4.0 mL glycerol, 0.5 g sodium acetate, and 10.0 g phthalic anhydride.
2. Carefully heat the mixture with a low flame, starting at the top of the contents and moving down toward the bottom as the mixture melts. Remember to point the test tube towards the back of the fume hood for safety reasons. CAUTION Excessive heating during step 2 can cause the hot contents to spurt out. If the hot liquid contacts the skin, severe burns result.
3. Continue heating until the melt appears to boil, and then continue heating for 5 minutes. Sufficient heating is required to produce a nonsticky product but excessive heating turns the product into a brittle amber material.
4. If desired, place a clean and dry coin into the aluminum dish used for a mold.
5. Carefully pour the hot liquid into the mold.
6. Allow the material to cool until the end of the laboratory period.
7. After the material has cooled, peel the mold from the cooled polymer and describe its appearance.

D. Cross-linked polyvinyl alcohol aka Slime!

CAUTION: The poly(vinyl alcohol) is a fine dust which you should avoid inhaling but you will only use it in solution.

1. Measure 50 mL of poly(vinyl alcohol) solution into a paper cup or small beaker and observe its properties. Vinyl alcohol does not exist. Poly(vinyl alcohol) is prepared by first forming poly(vinyl acetate) from vinyl acetate following by hydrolysis to the alcohol.
2. Measure 7-8 mL of sodium tetraborate solution into another cup or beaker and observe its properties. Add a few drops of food coloring at this step, if you wish.
3. Pour sodium tetraborate into the poly(vinyl alcohol) solution while stirring vigorously with a wooden stick. The borate forms a complex structure called tetraborate, $B_4O_5(\mathrm{OH})_4^{2-}$, that links the poly(vinyl alcohol) polymer strands together by hydrogen bonds.
4. Wearing safety gloves, examine the properties of the cross-linked polymer. See how far the polymer will flow from your hand. Is the

flowing endothermic or exothermic?

E. Silicone Plastic

Silicone plastic, commonly called Silly Putty, can be successfully approximated with Elmer’s Glue instead of silicone oil. You may each make your own silly putty if you wish and if you want to keep it, bring a Ziploc bag – great finger exerciser, stress reliever, bouncy ball etc.

1. Mix the food coloring with 30 mL of 50% Elmer’s Glue solution.
2. Add the 5 mL of 4% sodium tetraborate (Borax) solution and stir for 2 minutes in the cups provided.
3. Wearing your safety gloves, roll around the lump in your hands for two minutes, after which time it will cease to be sticky.
4. Examine the properties of this inorganic polymer.
5. If you wish to keep your silly putty, bring a Ziploc bag to lab.